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Bulletin 680

Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries— A Manual

By Joseph M. Kuchta

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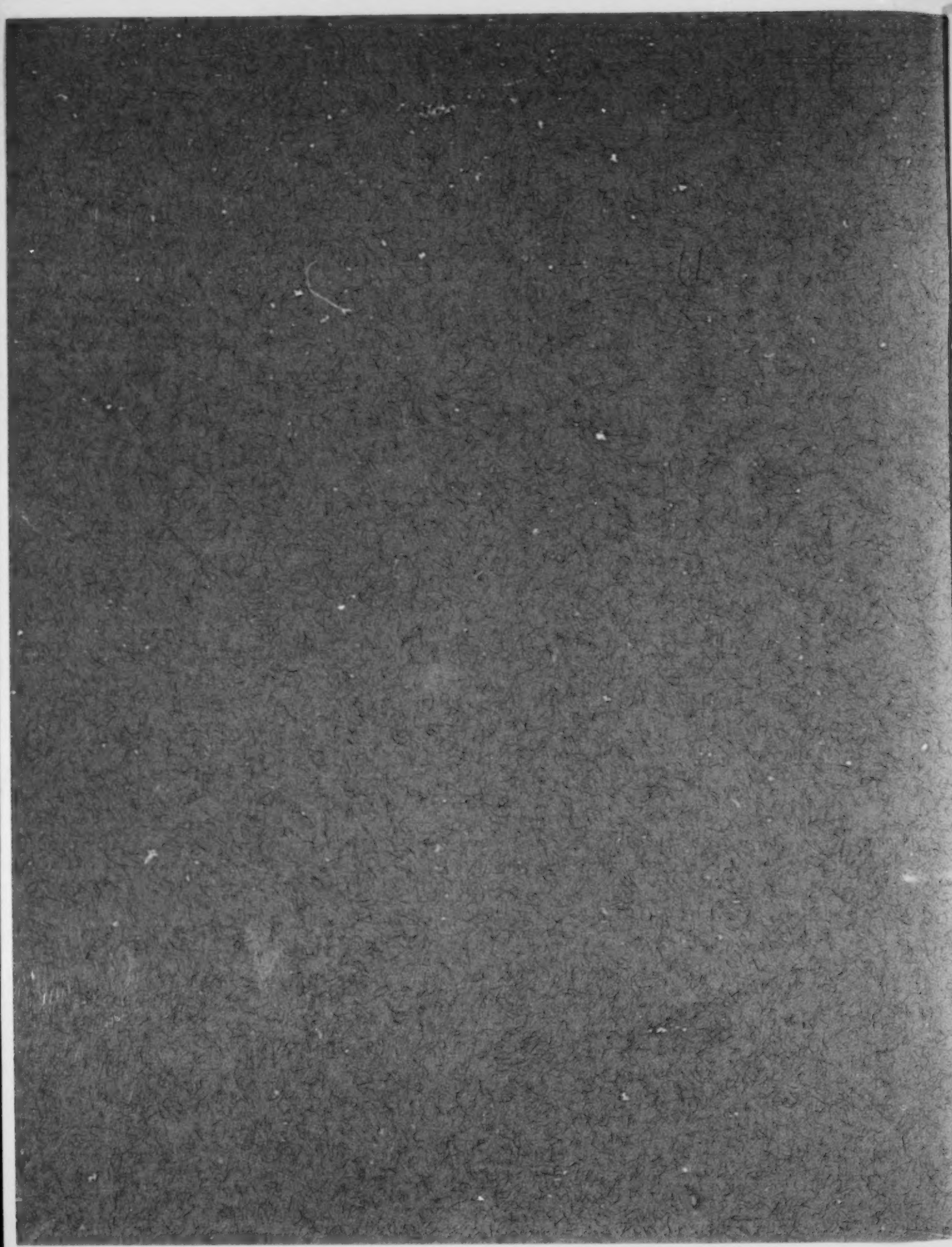

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UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

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159-315 O - 86 - 1

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environment and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

Library of Congress Cataloging in Publication Data

Kuchta, J. M.
Investigation of fire and explosion accidents in the chemical, mining, and fuel-related industries.

(Bulletin/U.S. Dept. of the Interior, Bureau of Mines; 680)

Bibliography: p. 68

Supt. of Docs. no.: I28.3:680

1. Chemical industries—Fires and fire prevention. 2. Mine fires. 3. Fuel—Fires and fire prevention. 4. Explosions. I. Title. II. Series: Bulletin (United States. Bureau of Mines) ; 680.

TH9445.C47K8 1985 660.2'804 85—600188

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, DC 20402

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INVESTIGATION OF FIRE AND EXPLOSION ACCIDENTS IN THE CHEMICAL, MINING, AND FUEL-RELATED INDUSTRIES—A MANUAL

By Joseph M. Kuchta[1]

ABSTRACT

This Bureau of Mines manual is oriented to the technical needs of an investigation of fire or explosion accidents and includes various practical and theoretical information that is needed in analyzing accidents or evaluating conditions that might lead to an accident. It is applicable to accidents in the chemical, mining, transportation, and other fuel-related industries. Specific procedures for conducting an accident investigation are outlined, and various guidelines are given for developing the fire or explosion evidence. Ignitability, flammability, and physicochemical data are presented for over 500 combustible gases, liquids, and solids; empirical and theoretical expressions are also given for extrapolating the behavior of combustible-oxidant-diluent systems to various environmental conditions. In addition, various data pertinent to damage analysis are summarized to facilitate the task of the investigator in developing plausible accident scenarios.

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INTRODUCTION

Accidental fires and explosions generally occur when combustibles are produced, transported, or utilized in a hostile environment or under unsafe conditions. Proper investigation of such accidents is essential for determining their cause and assessing life or property loss and for preventing their recurrence. This requires a methodical and thorough investigation, knowledge of the basic properties of pertinent materials, understanding of the ignitability and flammability characteristics of the combustible-oxidant system, and understanding of combustion or explosion principles. The main purpose of this manual is to summarize useful guidelines and provide data that are frequently needed for investigating fires and explosions or evaluating conditions that may be conducive to such events. It is applicable to flammable liquids, gases, and solids that may be encountered in the chemical, mining, transportation, or other mineral-fuel-related industries.

Among the most widely used publications on the flammability characteristics of combustibles are the Bureau's bulletins by Zabetakis (*110*)[2] and Coward (*11*). However, these bulletins are limited to liquid and gaseous combustibles, and reference must be made to other publications for similar information on combustible solids. Furthermore, other combustion and physicochemical data that may be required in a hazard analysis are even more widely scattered throughout the literature. Some safety handbooks, such as that of the National Fire Protection Association (NFPA) (*72*), provide various data on many combustibles, but the information is not sufficiently comprehensive for the analysis of an accident; also, the data are rather meager for mining applications. This manual attempts to overcome the scope limitations of the earlier Bureau bulletins and brings together many other essential data for characterizing the reactivity and damage potential of various classes of combustibles.

Ignitability, flammability, and thermochemical data are presented for over 500 combustible gases, liquids, and solids. The main groups of combustibles include hydrocarbons and substituted hydrocarbons, gasolines and lubricating fluids, coals and other mine-related combustibles, and various agricultural, chemical, plastic, metallic, and carbonaceous solids; explosives are beyond the scope of this report, although certain data are included for comparison. Most of the ignitability and flammability data are taken from Bureau publications, but other authoritative sources were also relied upon to complete the data. Generally, the various data represent the most acceptable or conservative values from the standpoint of safety, unless otherwise specified.

This manual is organized to facilitate the task of finding the particular data or information of interest. The initial section outlines specific procedures for accident investigations; the second section presents pertinent definitions and basic concepts for understanding combustion data; the next sections discuss the large compilation of combustion data presented for various combustible classes; and the final section deals with the damage analyses of fire and explosion accidents. The main data compilations are given in summary tables which provide easy access to many useful properties of the combustibles; additional data in the text expand on this data base. Limitations of the experimental data are discussed, and both empirical and theoretical guidelines are given for extrapolating the data to other environmental conditions and for estimating the energy or damage potential of a combustible-oxidant system. Other publications can be referred to for more fundamental knowledge of the combustion processes discussed in this report (*21, 24, 66, 93, 98*).

ACKNOWLEDGMENTS

The Bureau of Mines data in this manual represent selected contributions of various research groups of the Pittsburgh Research Center over at least four decades. Particular acknowledgment is given to the members of the fire or explosion groups with whom the author was associated in advancing the art of safety technology. The author is especially indebted to Drs. Michael G. Zabetakis, presently with the University of Pittsburgh, Pittsburgh, PA, and David S. Burgess, retired, who provided practical and theoretical guidance in the author's research; Aldo F. Furno, Michael J. Sapko, Ralph W. Cato, and George H. Martindill, who conducted many of the ignitability and flammability studies; and Dr. Martin Hertzberg, who collaborated most recently in developing flammability concepts for combustible gases and dusts. Acknowledgment is also given to John Nagy and coworkers for their important contributions in the area of dust explosions.

PROCEDURES FOR ACCIDENT INVESTIGATION

INITIAL ACTIONS

A formal investigation of an accidental fire or explosion is ordinarily conducted by a cadre of technical specialists and responsible officials. In industrial cases, this typically includes plant representatives, safety officers, fire department officials, and experts in combustion and engineering technologies. Where military or civilian Government agencies have jurisdiction, as in mining and aircraft disasters, the makeup and procedures of the investigating team will necessarily be determined by the requirements of the proper agency. In all cases, the team members should meet as soon as possible to obtain a briefing of the accident, decide upon the plan(s) of action, and establish task groups to accomplish various specific objectives. The head of the investigating team must organize and coordinate these actions to ensure that all aspects of the accident are

[2]Italicized numbers in parentheses refer to items in the list of references preceding the appendix.

properly covered. Initial actions that should be taken are—
1. Isolation of accident site.
2. Protection of evidence.
3. Recovery of material evidence.
4. Photographic documentation of evidence.
5. Documentation of witness accounts.

Isolation of the accident site is important to ensure recovery and protection of all available evidence and also to minimize unnecessary human exposure to any hazards that may still exist. Confined areas should be entered with caution since flammable or toxic gases may be present even after a fire. Before removal of any fire or explosion debris, the accident area should be photographed, including detailed color exposures of suspect items; also, tagging and mapping of damaged materials is common practice to avoid subsequent confusion. Where materials are fragmented by an explosion, areas beyond the accident site may have to be searched to recover the items. Those involved in these early actions must protect the evidence from being inadvertently tampered with, destroyed, or lost.

Equally important are the accounts of all available witnesses, including those present in the immediate or remote vicinity of the accident and those who arrive later on the scene, such as firemen and medical personnel. Such accounts should be obtained as soon as possible after the accident with the witness calm and at ease. Of particular interest is what the witness saw, heard, or sensed before and after the accident, as well as the proximity and activity of the witness during the course of events. All witness accounts are recorded in writing, and further interrogations are made when necessary in developing the evidence.

INVESTIGATIVE PROCEDURES

The procedures for investigating accidents will vary from one case to another, but all involve the basic elements of factfinding and problem solving to develop a credible accident scenario. Frequently, the cause of an accident is difficult to pinpoint because the available evidence is incomplete, inconsistent, or only circumstantial. Therefore, it is necessary to have a methodical plan for accumulating and developing evidence, both direct and indirect, that will be needed to fully explain an accident. A recommended plan of investigation is summarized herein, including—
1. Accumulation of background information.
2. Inspection of accident site.
3. Interrogation of witnesses.
4. Development and analysis of evidence.
5. Conclusions and report.

Background Information

At the outset, the investigator should obtain all available background information pertaining to the accident. This includes a description of the accident site and systems or operations involved, conditions and events that led to the accident, performance histories of any suspect systems, and all the available evidence accumulated from any initial actions. Particularly important are what combustibles and oxidants were present and what abnormal or hazardous conditions existed that might account for the accident. A close examination should be made of witness accounts, maintenance records, operational logs and manuals, weather reports, previous accident reports, and other records that may be helpful in developing the evidence. Recent changes in equipment, procedures, or operating conditions can be especially significant. The investigator must be open-minded and reserve any judgment until all human and material factors have been fully considered.

Site Inspection

Inspection of the accident site is one of the most important steps in obtaining physical evidence. Initially, an examination is made of the overall operation involved and damage sustained by the immediate and remote surroundings. The investigator should prepare an areal map on which the damage patterns, including fragments from any explosion, can be spatially defined. Subsequently, a detailed examination is made to obtain evidence on the apparent origin, propagation, and localized damage of the fire or explosion. This should include examination of all electrical and mechanical systems as possible problem sources. The area with the greatest damage is generally given the most initial attention because it is normally the source of the combustible. The following items are typical of the evidence which an investigator must uncover or consider:
1. Combustible quantity, distribution, and consumption.
2. Combustible leakage or spillage.
3. Open flame heat sources.
4. Electrical and mechanical heat sources.
5. Chemical-type heat sources.
6. Fire condition, propagation, and damage.
7. Explosion condition, propagation, and damage.
8. Material and system failures.
9. Operator or human error.

Witness Interrogation

After inspection of the accident site, the investigator should review the witness accounts for consistency with the physical evidence and interrogate any witnesses, as may be necessary, to help clarify any inconsistencies. It is important to recognize that witness accounts of accidents are subject to sight and hearing limitations in resolving a rapid series of events. For example, it is not unusual for a witness to claim hearing two explosions when only one actually occurred, or to give poor estimates of distances to an object or between two moving objects because of confusion during an accident; similarly, the size and velocity of moving objects are frequently exaggerated. Therefore, witnesses should be requested to qualify their observations relative to known landmarks and events to help establish their evidence spatially and temporally. Interrogation of maintenance personnel on any equipment involved should always be included as a standard practice. At this time, the investigator needs to decide what facts are known and what evidence must be substantiated or developed.

Evidence Development and Analysis

Ideally, sufficient evidence should be accumulated to explain all phases of an accident, including the specific cause. The required physical evidence will vary with the type of accident. In fires or explosions, it is particularly important to account for the combustible source, probable ignition source, resultant propagation, and observed damage. The available evidence is analyzed by developing and testing hypotheses that may explain the sequence of events; any assumptions must be consistent with the fully established evidence and basic scientific principles. Some

important considerations in developing the evidence are reviewed in the following paragraphs.

1. Combustible Source.—In a fire situation, various combustible classes can be consumed as the fire spreads. These include ordinary combustible solids or dusts (class A), combustible liquids and gases (class B), combustibles of electrical equipment (class C), combustible metals (class D), or other miscellaneous materials; combustible fire classification is that of NFPA (*72*). Fires that spread rapidly are usually attributable to combustible gases, vapors of highly volatile liquid or solid combustibles, or finely divided solids that are highly flammable. Those that can be initiated without an external heat source are likely to involve pyrophoric, hypergolic, water-reactive, or self-heating combustibles. Soot formation is evidence of hydrocarbon or organic fuel fires, and extremely high temperatures can be indicative of combustion with high-energy fuels or high-strength oxidizers. Any widespread fire will always be accompanied by a wide distribution or dispersion of combustible.

In gaseous or dust explosions, the combustible sources are only those that can form flammable gas, vapor, or dust concentrations in the particular oxidant atmosphere and temperature environment; this implies some degree of confinement. Prime combustible suspects are fuel gases, low-flash-point liquids, gassy solids, and dispersed flammable dusts. The ignitability and flammability characteristics of the suspect combustible-oxidant system should be examined for supporting evidence. When possible, samples of the combustible system are taken for analysis to verify compositions. A likely combustible source also has to be present in sufficient concentration to account for the observed explosion pressure damage. The investigator must realize that relatively low combustible concentrations can be hazardous and that even an "empty" fuel tank may contain sufficient combustible vapor to account for the explosion. Where damage is unusually severe, combustible systems capable of detonation are to be suspected.

2. Ignition Source.—The possible sources of ignition can include electrical, mechanical, chemical, or nuclear forms of energy. Some of the specific types are (1) electrical arcs or sparks from lightning, static electricity, and defective electrical equipment; (2) hot surfaces from mechanical friction, electrical resistance heating, aerodynamic heating, and any vessel or reactor heating; (3) hot gases or flames from pilot burners, combustor exhaust systems, and gaseous compressor systems; and (4) chemical heating from pyrophoric, hypergolic, and spontaneous or self-heating reactions. Most fires or explosions are initiated by electrical sources. The static electricity source should be especially suspected as possible in the pumping of liquids or dusts and similar operations where triboelectrification can occur; this hazard will be greatest in the presence of plastic or nonconductive materials. The most common type of chemical self-heating involves slow oxidation and may be encountered with many combustibles of animal or vegetable oil origin and such ordinary combustibles as coal and charcoal. Self-heating, pyrophoric, and hypergolic ignitions require no external heat source.

In some accidents, the ignition source may be evident from localized heat damage such as weldlike fusion of metals from electrical arcing, discoloration or wear of metals from mechanical friction, and melting of metal materials due to abnormal process temperatures. The heat source in other cases, including electrostatic, self-heating, and hot gas ignitions, is not usually identifiable from the fire or explosion damage; therefore, the investigator must rely upon circumstantial evidence in such cases.

Both the nature of the available heat source and the physical state of the suspect combustible must be considered in determining the ignition source. For example, a flammable gas (such as hydrogen) may have a very low ignition energy but a relatively high ignition temperature; or a flammable liquid spray can have a high ignition energy compared to that possible with homogeneous vapor-air mixtures. Similarly the ignition energy requirements for a solid (such as coal dust) can be excessive for large particles, in which case the ignition temperature can be of greater significance. A proper assessment requires reference to ignition property data.

3. Propagation.—Propagation of a fire or explosion is deduced from the available physical evidence and known flammability properties of the combustible-oxidant system. Gas or dust explosions will propagate only into areas where flammable combustible-oxidant mixtures have accumulated but may then initiate fires of other combustibles. In comparison, fires do not require uniform combustible-oxidant mixtures and can propagate into areas where any concentration of combustible exists; also, the gaseous fire products may be flammable and produce an explosion in a confined environment, as in some coal mine disasters.

To fully characterize the propagation of fires or explosions, the investigator needs to define the consumption rates (burning rates) of the reactants and their flame propagation rates (flame speeds or flame spread rates). Such information may be available in the literature but is necessarily limited to certain temperature, pressure, and combustible-oxidant conditions. Therefore, it is often necessary to extrapolate laboratory data to conditions of interest by the prudent use of empirical rules or laws.

Typically, flame propagation rates of common hydrocarbon gas-air explosions are of the order of several meters per second, or about eight times the burning velocity of the particular mixture composition. In comparison, fires are usually associated with much lower spatial propagation rates, especially in the burning of bulk liquids and solids. However, all fires or flame propagation can accelerate by increased ventilation, turbulence, or wind effects, as in flight vehicles, ventilation ducts, or mine tunnels. The flame spread can be even greater when the fires are supported by strong buoyant forces, such as in a building stairwell or an elevator shaft. Highest propagation rates with liquids and solids will occur when they are finely dispersed or flash vaporized.

Very high propagation rates of the order of a 1,000 m/s or more are possible when deflagrations develop into detonations. Detonations are most likely to be encountered in combustion involving high pressures, high oxygen concentrations, or high-energy fuels. Even ordinary fuel-air systems are capable of detonation, but these require stronger ignition sources or longer flame runup distances.

4. Fire Damage.—Fire damage is largely attributable to the exposure of materials to excessive temperatures or heat. Fire temperatures of ordinary combustibles in air will generally be 1,000° to 2,000° C, but temperatures can be much higher in oxygen or with more exotic combustibles. An investigator's analysis of the fire damage should include consideration of such factors as—

1. Combustible loading and ventilation.
2. Size, shape, and distribution of materials.

3. Proximity and exposure duration of materials.
4. Fire temperatures, burning rates, and heat release.
5. Fire resistance properties of damaged materials.

Maximum fire temperatures will normally be evident where the air or oxygen ventilation is optimum for combustion, whereas the heat flux or heat release will depend additionally upon the combustible loading and burning rate. Most constructional materials cannot withstand the fire temperatures and heat loading from a fully developed hydrocarbon or carbonaceous fuel-air fire. Materials of low fire resistance, such as those having low melting points or ignition temperatures, will be consumed or largely destroyed; this will be especially the case for fine wires, sheet materials, or finely divided substances. However, one should also expect highly fire-resistant materials to fail when the fires are of severe intensity. On the other hand, even paper will not ignite if its exposure time to flame is too short or if its proximity to the heat source is too remote.

Ordinarily, material failures will be severest in fires involving large combustible loadings (as in fuel storage facilities), high ventilation or turbulence levels (as in aircraft flight applications), high oxidant concentrations (as in hyperbaric chambers), or high-energy combustibles (as in space rocket applications). Few materials will survive a torchlike fire, particularly one in oxygen; such intense fires are often evidenced by the erosion and fusion of metals. Similar metal damage can also occur in electrical fires, although any metal fusion due to electrical arcing will be more localized and display beadlike welds. Damage to powered equipment (motor, pumps, compressors, etc.) is often attributed to electrical or mechanical malfunctions but can be a result of the fire itself. Temperature limitations of materials and the extent of their fire exposure should be considered in making the fire damage assessment.

5. Explosion Damage.—Explosion damage is caused by the high pressures and winds that are generated by the sudden release of chemical or physical energy. Although the damage analyses may vary with the complexity of the explosions, they should at least include consideration of the following important items:

1. Combustible loading and confinement.
2. Explosion pressures, propagation rates, and energy release.
3. Pressure limitations of containment materials.
4. Nature of containment failure.
5. Blast wave or far-field effects.
6. TNT energy equivalence.

The most common explosions will involve the ignition of flammable vapor-air mixtures in a confined environment. If near-stoichiometric mixtures are present, the explosion pressure in a fully confined system can be approximately eight times the initial pressure ($P_2/P_1 = 8$). Such internal pressure loading will be evidenced by the rupture of the container unless it can sustain the explosion pressure. Similar damage can result in the absence of combustion, as in the failure of an overpressurized steam boiler, compressed gas cylinder, or cryogenic liquid receiver; the rupture of an evacuated chamber (implosion) or a decompressed aircraft compartment also falls into this category. Other explosions may produce damage from a combination of physical and chemical energy release. These include fuel tank explosions under high-impact conditions, furnace explosions of molten metal and water or combustible liquids, and boiling liquid-expanding vapor explosions (Bleves). In all cases, the explosion damage will be more severe when combustion involves high oxygen concentrations, elevated pressures, or highly turbulent environments. Detonations are more likely to occur in these situations, in which case the explosion pressure rise ratio (P_2/P_1) can be of the order of 18 to 1 for gaseous systems, or several orders of magnitude greater for condensed explosive systems.

Containment material failure or near-field damage is largely determined by the nature of the pressure loading, the degree of confinement, and the pressure or mechanical limitations of the container, fasteners, and adjacent materials. Explosions in highly confined systems have high damage potential because near-theoretical pressures can develop before any containment failure. In comparison, even an ordinary oven or building can sustain an explosion if it is adequately protected with large pressure relief panels or vent areas. Explosion venting guidelines are available for predicting the safe pressure limits of containments as a function of vent area. The containment failures in ordinary explosions will be evidenced by material stretching or thinning out (tension failure), whereas those in detonations will tend to be more severe and cleaner breaks (shear failure); an implosion will be characterized by a compression-type failure. The pressure limitations of a container can be estimated from a knowledge of the elastic limit or ultimate strength of the container material. However, one must allow for the fact that the dynamic stress is about two to three times the static stress for plastic deformation; pressure ratings of commercial vessels are usually specified for static-type loadings. Any container fragmentation should be expected to be greater for brittle materials than for highly ductile types.

Far-field effects are associated with the explosion damage that results from air blast waves and flying fragments. These effects will be especially evident where strong containments fail owing to detonations or highly energetic deflagrations. Here, the investigator should estimate the TNT energy equivalent of the exploding system from the available chemical energy or potential useful work (gas expansion); apply the cube-root scaling law for predicting blast pressures at any distance from any mass equivalent of TNT; and correlate the estimated blast pressures to published damage thresholds for structural and biological targets. Generally, one can expect a peak overpressure of 1 to 2 psi to cause the failure of most light structural materials, such as nonreinforced wood siding, corrugated steel paneling, or masonry block walls. In comparison, much higher overpressures can be tolerated when the structural design is reinforced, particularly for materials of good ductility. As a rule, pressure thresholds for far-field damage (external loading) will be greater than those for near-field damage, such as a containment failure (internal loading). Where condensed-phase detonable systems are involved, crater formation will also be possible besides far-field damage.

Conclusions and Report

All the available direct and indirect evidence is finally reviewed for accuracy and reliability to define the most likely sequence of events and probable cause(s) of the accident. Any hypotheses proposed to explain the accident should be logically and technically consistent with the

established evidence. A proper analysis will include consideration of both material and human factors. To complete the investigation, the investigator should prepare a summary report on the accident. This should include a description of the accident, accounts of witnesses, evidence from field inspection, analysis of evidence, and development of accident scenario to explain the cause of the accident. Most importantly, system malfunctions and hazardous conditions should be identified, and specific recommendations should be made to prevent recurrence of the accident, including both operative and protective measures.

THEORY AND DEFINITIONS

PHYSICAL GAS LAWS

Pressure-volume-temperature (PVT) relationships are important in determining material balances for a gaseous system. In most cases, one can assume *ideal gas behavior* and define the initial (1) and final (2) states of a gas as follows:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad (1)$$

where T_1 and T_2 refer to absolute temperature, such as in kelvins (K). The general form of the ideal gas law is given by

$$PV = nRT = \frac{W}{M}RT \qquad (2)$$

$$\text{or} \quad P = \frac{W}{V}\frac{RT}{M} = \rho\frac{RT}{M}, \qquad (3)$$

where n, W, M, and ρ are the moles, weight, molecular weight, and density of the gas, respectively; R is a universal gas constant equal to 1.987 cal/(K·mol), 0.08205 L·atm/(K·mol), or 8.314 J/(K·mol) depending upon the P-V units. Thus, the volume of gas will vary directly with absolute temperature and inversely with total pressure. In calculating the moles of gas, it is useful to know that the *molar volume* of any ideal gas will occupy 22.414 L at 1 atm and 273 K (0° C).

For mixtures of ideal gases, the total pressure (P_t) is equal to the sum of the component partial pressures ($P_t = p_1 + p_2 + \ldots$) and proportional to the total number of moles ($N_t = n_1 + n_2 + \ldots$). Hence, the mole fraction (X) of a gaseous component (i) is

$$X_i = n_i/N_t = p_i/P_t, \qquad (4)$$

and 100 X_i gives the mole or volume percent. For the vapors of ideal liquids, one uses Raoult's law:

$$X_i \text{ (liquid)} = n_i/N_t \text{ (liquid)} = p_i/p_i^\circ \text{ (vapor)}, \qquad (5)$$

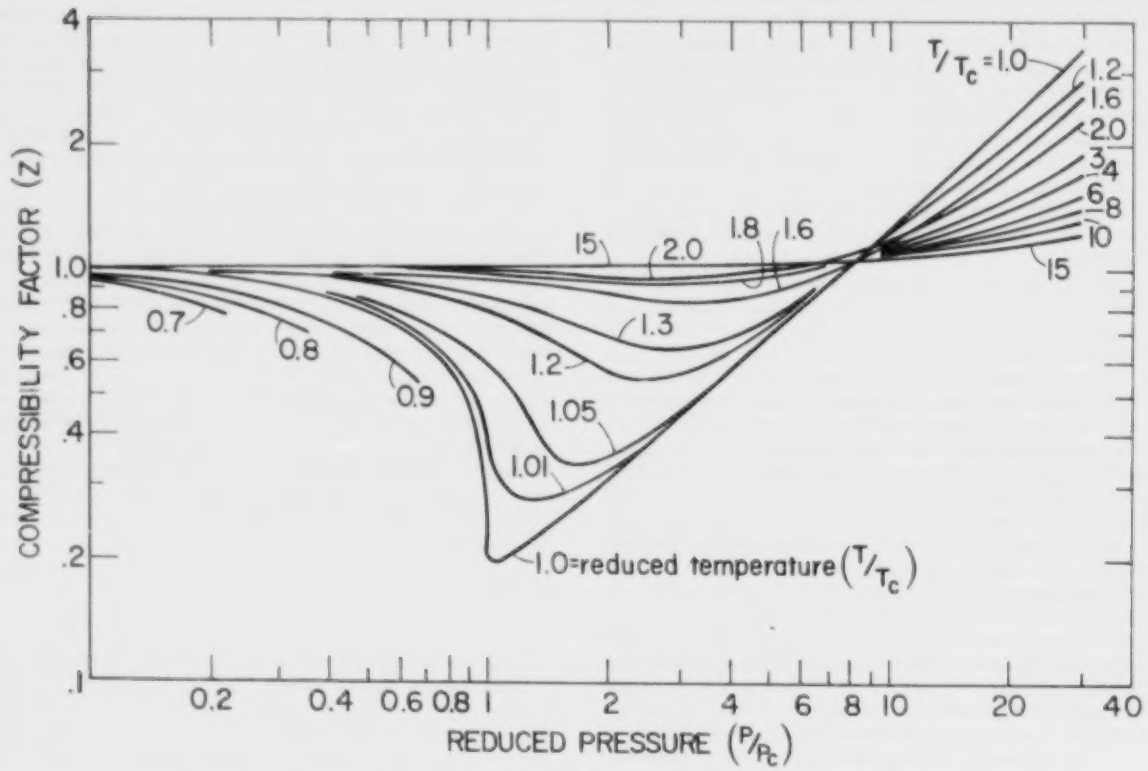

Figure 1.—Compressibility factor as a function of reduced pressure and reduced temperature.

where p_i is partial pressure of the i^{th} component in solution, p_i° is the vapor pressure of the pure component, and X_i is its mole fraction in solution.

Real gases deviate from ideal behavior, particularly when subjected to high pressures or cryogenic temperatures. In such cases, other equations must be used to determine the P-V-T relationships, such as the equation

$$PV = n Z RT, \tag{6}$$

where Z is a compressibility factor and depends upon the critical properties of the gas (P_c, T_c, and V_c). A fair approximation of the Z factor can be obtained for most gases from the generalized compressibility curves (*34*, p. 479) shown in figure 1 in terms of reduced pressure ($\pi = P/P_c$) and reduced temperature ($\Theta = T/T_c$); gases difficult to liquefy, such as hydrogen, give a more complex behavior. Critical states and vaporization properties are given in table 1 for a number of common gases and liquids (*27*, p. 502).

Table 1. — Critical states and vaporization properties of common gases or liquids (*27*, p. 502)

Substance	Boiling point (T_b), K	Heat of vaporization at T_b, kcal/mol	Critical temperature (T_c), K	Critical pressure (P_c), atm
Acetylene	184.7	NA	309.1	61.7
Ammonia	239.8	5.56	405.5	111.5
Benzene	353.3	7.40	561.6	47.7
n-Butane	272.6	5.30	426.0	36.0
i-Butane	263.0	5.08	407.1	37.0
Carbon dioxide	NA	NA	304.1	72.9
Carbon monoxide	81.1	1.41	134.4	34.6
Chlorine	239.5	4.80	417.0	76.0
Ethane	185.9	3.80	305.2	48.8
Ethylene	169.3	NA	282.8	50.7
Ethyl alcohol	351.6	9.40	516.2	63.1
Hydrogen	20.3	.216	33.2	12.8
Hydrogen bromide	206.2	3.95	363.0	84.0
Hydrogen chloride	189.5	3.60	324.5	81.6
Hydrogen cyanide	299.2	5.70	458.6	56.9
Hydrogen sulfide	213.4	4.49	373.5	88.9
Methane	111.7	1.95	191.1	45.8
Methyl alcohol	337.8	8.41	513.2	98.7
Nitrogen	77.3	1.36	126.0	33.5
Nitrogen oxide	121.4	NA	179.0	65.0
Nitrogen dioxide	NA	NA	431.0	99.0
Oxygen	90.2	1.61	154.3	49.7
Propane	231.0	4.50	369.9	42.0
Propylene	226.2	NA	364.8	45.0
Sulfur dioxide	263.2	6.08	430.3	77.7
Water	373.2	9.717	647.3	218.2

NA Not available.

STOICHIOMETRY

Combustion material balances will vary with the composition and concentration of the reactants and the nature of the products at the reaction conditions. Theoretically, the maximum heat release should occur at the *stoichiometric concentration* (C_{st}) that defines the optimum molar concentration of combustible for complete reaction with the particular oxidant; fuel-lean mixtures suffer from oxidant dilution and fuel-rich mixtures from incomplete reaction. The stoichiometry for complete combustion of a simple hydrocarbon in oxygen is given by the expression

$$C_cH_h + \left(c + \frac{h}{4}\right) O_2 \rightarrow c\,CO_2 + \frac{h}{2}\,H_2O, \tag{7}$$

and for substituted hydrocarbons by the general expression

$$C_cH_hO_mN_nX_x + \left(c + \frac{h\text{-}x\text{-}2m}{4}\right) O_2 \rightarrow c\,CO_2 + \left(\frac{h\text{-}x}{2}\right) H_2O + x\,HX + \frac{n}{2}\,N_2, \tag{8}$$

where X is any halogen atom. Thus, the C_{st} of methane (CH_4) in oxygen $\left(\frac{100}{1 + c + h/4}\right)$ is 33.3 mol pct. For combustion in air,

$$C_{st}\,(\text{in air}) = \frac{100}{1 + 4.773\left(c + \frac{h\text{-}x\text{-}2m}{4}\right)}\ \text{mol pct}, \tag{9}$$

where 4.773 is the reciprocal of the molar oxygen concentration in air (0.2095). By this equation, one obtains a C_{st} of 9.48 mol pct for methane in air. Similar expressions may be derived for incomplete or other combustion reactions in which H_2, CO, NO_2, or other possible products are assumed. For example, if NO_2 instead of N_2 is an assumed product, the oxygen term in equations 8 and 9 would be

$$\left(c + n + \frac{h\text{-}x\text{-}2m}{4}\right).$$

The volume percentages can be converted to a weight basis from a knowledge of the densities or molecular weights of the mixture components. As an example, the fuel-air weight ratio (F/A) of a stoichiometric mixture is given by

$$(F/A)_{st} = \frac{M}{28.97}\left[\frac{C_{st}\,(\text{vol pct})}{|100 - C_{st}\,(\text{vol pct})|}\right], \tag{10}$$

where M is the fuel molecular weight and 28.97 is the air molecular weight. Pertinent properties of air are summarized in tables 2 and 3.

Table 2. — Major components of dry air (*43*, *105*)

Constituent	Molecular weight	Density (0° C), g/L	Specific heat (20° C), cal/(g·° C)	vol pct
Nitrogen	28.01	1.251	0.249	78.09
Oxygen	32.00	1.429	219	20.95
Argon	39.94	1.784	124	.93
Carbon dioxide	44.01	1.977	200	.033
Air	28.97	{ 1.293 (0° C) } { 1.205 (20° C) }	240	100.0

Table 3. — Standard air atmosphere (*43*)

Altitude ft	Temperature, °C	Pressure, bars	Density, kg/m³
0	15	1.013	1.225
1,000	13	.977	1.190
5,000	5	.842	1.056
10,000	−5	.696	.905
15,000	−15	.571	.771
20,000	−24	.465	.654
30,000	−44	.301	.458
40,000	−55	.188	.300
50,000	−55	.116	.186
60,000	−55	.072	.115

THERMODYNAMIC RELATIONSHIPS

A knowledge of thermodynamic properties is essential in calculating the energy balance of a given system. The energy change may be in the form of work performed or heat transferred relative to the system surroundings. By the first law of thermodynamics (energy conservation), the energy change (ΔE) is

$$\Delta E = Q - W, \tag{11}$$

where Q is the heat absorbed (positive) and W is the work done by the system (positive); heat evolved or work on the system would be negative. For an *isothermal process* ($\Delta E = 0$), the total mechanical work ($W = \int PdV$) of expansion or compression of an ideal gas is

$$W = n\,RT\,\ln V_2/V_1 = n\,RT\,\ln P_1/P_2; \quad P_1V_1 = P_2V_2. \tag{12}$$

For an *adiabatic process* ($Q = O$), the total work ($W = -\int Cv\,dT$) is

$$W = n\,C_vT_1\,[1 - (P_2/P_1)^{R/C_p}];\ P_1V_1^{\gamma} = P_2V_2^{\gamma}, \tag{13}$$

where C_v and C_p are molar heat capacities, γ is C_p/C_v ratio, and their subscripts refer to constant volume (v) or constant pressure (p). Figure 2 shows how much greater the volume change of an ideal gas can be in an isothermal compression as compared to an adiabatic compression at various pressure ratios. In the adiabatic process, the temperature change is

$$T_2/T_1 = (V_1/V_2)^{R/C_v} = (P_2/P_1)^{R/C_p}. \tag{14}$$

Reactions may occur at constant volume or constant pressure. Under constant volume, where no mechanical work is performed ($W = O$), the heat change by equation 11 would be $Q_v = \Delta E$; at constant pressure, the heat change

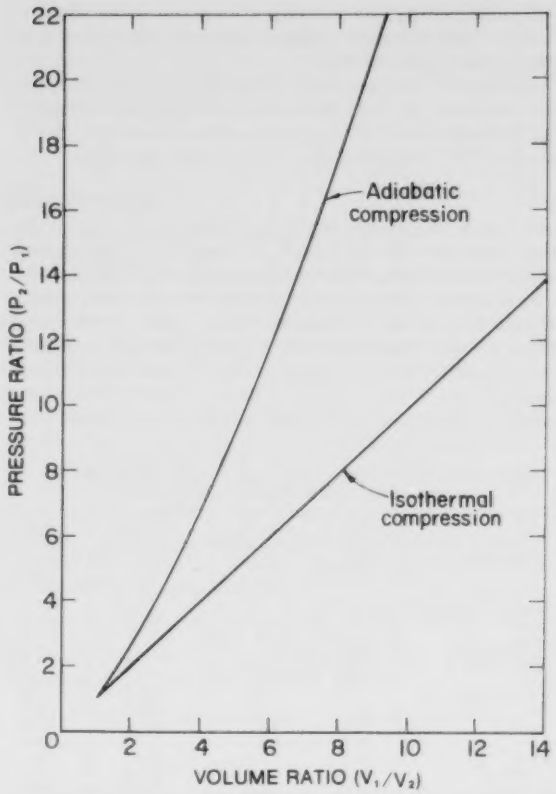

Figure 2.—Variation of pressure ratio with volume ratio in adiabatic and isothermal compression of an ideal gas.

is $Q_p = \Delta E + P\Delta V$. Since the heat content or enthalpy (H) of a system is

$$H = E + PV \tag{15}$$

and $\Delta H = H_2 - H_1 = Q_p$, the heat change at constant pressure becomes

$$\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n\,RT, \tag{16}$$

where Δn is the change in the moles of gas after reaction of the system. Equations 15 and 16 are very useful because most standard thermodynamic properties are at constant pressure. The molar heat content of a number of common product gases is given at various temperatures in table 4;

Table 4. — Heat content (enthalpy) of combustion product gases at various temperatures[1]

Temperature, K	Heat content, kcal/mol						
	H_2	O_2	N_2	CO	CO_2	H_2O	NO
298.16	0	0	0	0	0	0	0
400	.71	.72	.71	.71	.94	.82	.73
600	2.10	2.21	2.13	2.14	3.09	2.51	2.19
800	3.51	3.78	3.60	3.63	5.45	4.30	3.72
1,000	4.94	5.43	5.13	5.18	7.98	6.21	5.31
1,200	6.40	7.11	6.72	6.79	10.63	8.24	6.96
1,400	7.91	8.83	8.35	8.45	13.36	10.38	8.64
1,600	9.45	10.58	10.01	10.13	16.15	12.63	10.36
1,800	11.04	12.35	11.71	11.84	18.99	14.96	12.09
2,000	12.66	14.15	13.42	13.56	21.86	17.37	13.84
2,200	14.31	15.97	15.14	15.30	24.75	19.84	15.60
2,400	16.00	17.80	16.88	17.05	27.67	22.37	17.37
2,600	17.71	19.66	18.63	18.81	30.61	24.94	19.14
2,800	19.45	21.54	20.39	20.58	33.56	27.55	20.93
3,000	21.21	23.45	22.16	22.36	36.53	30.20	22.72

[1]Data from reference 28 rounded off to 2 decimal places.

298.16 is the reference zero enthalpy state. These data are derived from the heat capacity relationship at constant pressure, $C_p = dH/dT$; the corresponding relation at constant volume is $C_v = dE/dT$; C_v is usually obtained from the approximation $C_p - C_v = R$. The constant-pressure heat capacity data are particularly important in calculating the final temperature of a reacting system, as discussed in a later section.

In a chemically reactive system, the reaction may evolve heat (exothermic) or absorb heat (endothermic). The heat of reaction (ΔH) is indicated by the enthalpy change of the reactants from their initial state to the final or product state. Here, the enthalpy change can be calculated by use of the heats of formation (ΔH_f – kcal/mol) of each specie; the standard values are defined at 25° C (298 K) and 1 atm. This is illustrated below for the complete combustion of methane at constant pressure with water formed as a liquid (l) or vapor (g):

$$\begin{matrix} CH_4 & + & 2O_2 & \rightarrow & CO_2 & + & 2H_2O(l); & \Delta H_{298} = \\ -17.9 & & 0 & & -94.05 & & 2(-68.3) & \end{matrix} \quad (17)$$

-212.8 kcal/mol.

$$\begin{matrix} CH_4 & + & 2O_2 & \rightarrow & CO_2 & + & 2H_2O(g); & \Delta H_{298} = \\ -17.9 & & 0 & & -94.05 & & 2(-57.8) & \end{matrix} \quad (18)$$

-191.8 kcal/mol,

ΔH_f values are given below each specie, and ΔH is equal to the sum difference of ΔH_f (products) $- \Delta H_f$ (reactants); negative ΔH indicates heat is evolved. The variation between the ΔH values (-212.8 versus -191.8) is equal to the latent heat of vaporization of water, i.e.,

$$H_2O(l) \rightarrow H_2O(g); \Delta H_{298} = 10.5 \text{ kcal/mol}. \quad (19)$$

Essentially, the larger ΔH represents the gross heat of combustion (ΔH_c), and the smaller ΔH is a net ΔH_c that is most meaningful when one is concerned with the product state at flame temperatures. Standard ΔH_f and ΔH_c (net) values are compiled in the summary data tables that are presented for each class of combustibles; the ΔH_f values can be used to calculate the ΔH_c values for other reactions of interest.

If the reactions occur under constant volume (closed system), the heats of reaction would not include any PV work ($\Delta V = 0$) and would be defined by

$$\Delta E = \Delta H - \Delta n\, RT. \quad (20)$$

For example, the change in gaseous moles in equation 18 is zero and, therefore, $\Delta E = \Delta H$. However, in the case of equation 17 where $\Delta n = -2$,

$$\Delta E = -212.8 + 2 \times 1.987 \times 10^{-3} \times 298 = -211.6 \text{ kcal/mol}. \quad (21)$$

It is evident that unless Δn is large, differences between heats of reaction at constant volume and constant pressure will be small.

IGNITION PROCESSES

General Concepts

Ignition is usually considered to be a vapor-phase combustion reaction with the evolution of heat and emission of light that may or may not be visible to the naked eye. Such reactions are most often associated with the rapid oxidation of a combustible in air or oxygen. They may also occur with other oxidants, such as the halogens and nitrogen oxides, as well as without any oxidant when the combustible is capable of highly exothermic decomposition. The potential heat release for any reacting system can be calculated from thermodynamic considerations, but the combustion rate or intensity will depend upon the chemical kinetics at the reaction conditions. For example, in the constant-pressure reaction of hydrogen and oxygen,

$$H_2 + 1/2\, O_2 \rightarrow H_2O(g); \Delta H_{298} = -57.8 \text{ kcal/mol}, \quad (22)$$

the theoretical heat release is 28.9 kcal per gram of hydrogen. If this heat is produced rapidly and results in a branching chain reaction, high temperatures and flaming combustion are possible. However, if the heat is generated at a slow rate, as in a low-temperature oxidation process, flaming combustion is unlikely to occur unless the slow oxidation can initiate a self-accelerating reaction.

Most combustible-oxidant systems are not capable of sufficient self-reaction at ambient temperature to produce ignition. Generally, they require heating to some critical level by an external temperature or energy source. It is useful to consider the sources in terms of their spatial and temporal characteristics, as illustrated in figure 3. At one extreme (electrical sparks), the source is infinitesimally small and very high in temperature and heating rate; here, one is primarily concerned with energy density and the ignition energy. At the other extreme (heated vessels), the source is large, heating rate is very low, and temperature is also relatively low; here, one is mostly concerned with the concept of an ignition temperature. Thus, it is most meaningful to define ignition requirements in terms of energy for a highly concentrated heat source and in terms of temperature for a distributed heat source; an exception

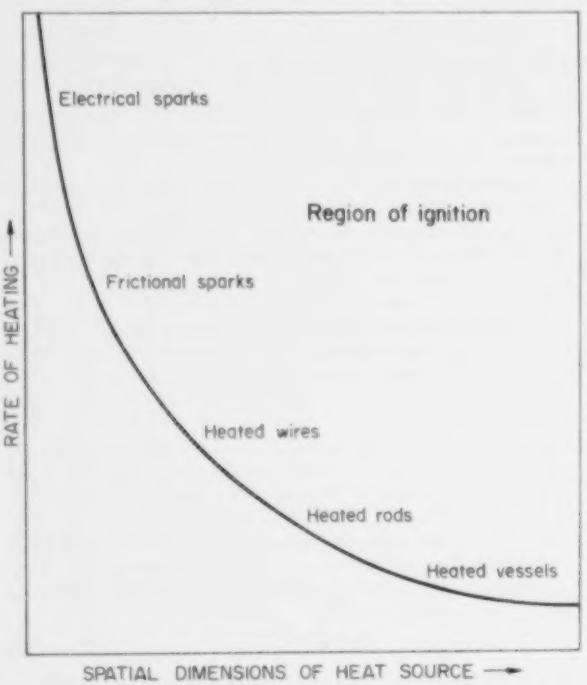

Figure 3.—Temporal and spatial characterization of various ignition sources.

is a large radiative heat source, which is usually defined in terms of energy.

Basically, ignition sources can be classified as either thermal or chemical types, the former being by far the most predominent type. In practice, electrical ignitions are treated as a separate category, although they are of a thermal nature; also, some ignitions are considered as thermal (self-heating) or chemical (pyrophoricity or hypergolicity) but are unique in that they do not require any external heat source. With this in mind, the various ignition sources may be categorized as follows:

Electrical ignitions:
1. High-voltage sparks or arcs.
2. Low-voltage sparks or arcs.

Thermal ignitions:
1. Hot surfaces:
   a. Heated vessels or walls.
   b. Heated wires or rods.
   c. Heated particles or frictional sparks.
2. Self-heating (spontaneous combustion).
3. Hot gases:
   a. Heated gas jets or pilot flames.
   b. Adiabatic or shock compression.
4. Thermal radiation.

Chemical ignitions:
1. Catalytic materials.
2. Pyrophoric and hypergolic mixtures.

Electrical Ignition

The simplest form of electrical ignition is a thermal process in which excessive surface heating is produced by the resistance to current flow in an electrical circuit. This resistance heating can be calculated from

$$E = VIt = I^2Rt, \quad (23)$$

where E is heat (J), V is potential difference (V), I is current (A), R is resistance (Ω), and t is time (s); Ohm's law (V = IR) is applied here. Ignitions by such heating may occur within a second or more and fall in the hot surface temperature category that is discussed later.

Other electrical ignitions involve sparks or arcs in which the energy approximates a point source and the heating duration may be as little as a fraction of a microsecond. These can be classified as a high-voltage or electrostatic type and low-voltage or break spark type. In the case of *electrostatic sparks*, they are formed when the electrical charge of a conductor is sufficient to bridge ("jump") the gap to another conductor or nonconductor. The energy of electrostatic discharge is given by

$$E = 1/2\ CV^2, \quad (24)$$

where E is the stored energy (J), C is capacitance of the charged conductor (F), and V is the potential difference (V); the capacitance is related to the electrical charge (Q) by C = Q/V, where Q is in coulombs. In the case of *break sparks*, they are formed when current-carrying conductors are abruptly separated to result in a collapsing field, such as when an electrical switch is opened. The energy of break sparks or arcs is given by

$$E = 1/2\ LI^2, \quad (25)$$

where L is the inductance (H). Although such energies can be orders of magnitude greater than those associated with capacitative spark discharges, the differences are not so noticeable when the breaking circuit involves a short gap length, as in the rapid separation of very fine wires.

Capacitative spark-type discharges are generally relied upon to determine the *minimum ignition energy* (MIE) of a combustible vapor-oxidant system. The MIE value occurs at an optimum spark gap length (electrode separation) and varies with temperature, pressure, and combustible-oxidant concentration; the optimum gap is referred to as the *minimum ignition quenching distance*. Figure 4 shows how the spark ignition energy can vary with the fuel-air weight ratio (F/A) for the butane-air system (*41*). Although stoichiometric butane combustion occurs at an F/A of 0.065 (3.12 vol pct), the MIE falls on the rich side of stoichiometric for this fuel. This figure also shows that whereas the minimum spark energy for ignition may be only a few tenths of a millijoule, it tends to be infinitely large as the mixture ratio approaches the limits of flammability.

The minimum ignition quenching distances in this context imply an optimum electrode design that maximizes

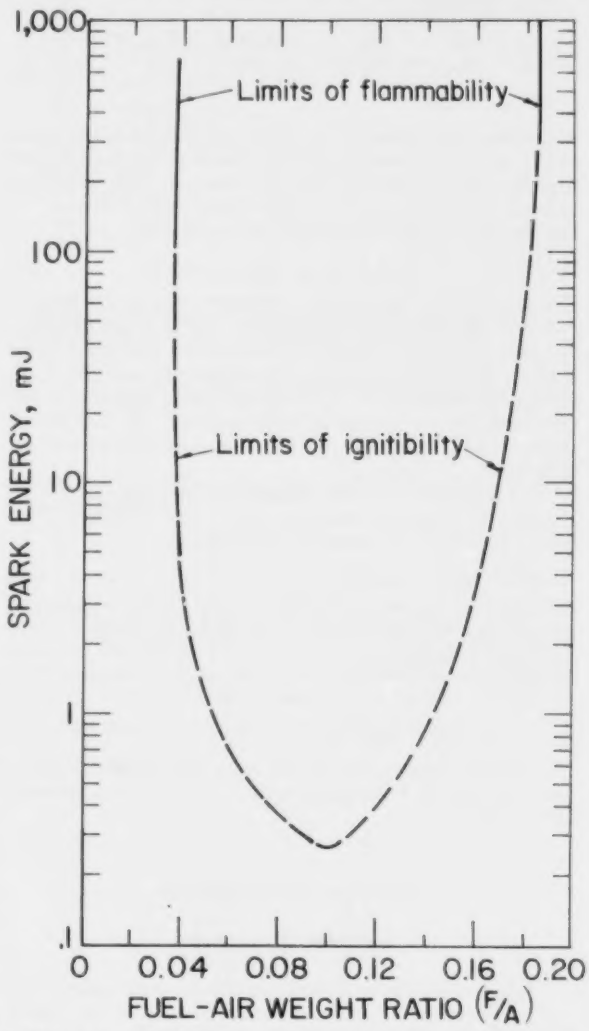

Figure 4.—Spark energy versus fuel-air ratio for ignition of n-butane-air mixtures at 25° C and 1 atm.

the spark energy efficiency in a quiescent mixture. They should not be confused with *minimum ignition quenching diameters* since these involve flowing mixtures and larger quenching surfaces; quenching diameters are roughly 1-1/2 times greater than corresponding quenching distances for many ordinary fuels, largely because of greater heat losses. In contrast, the so-called *maximum experimental safe gaps* involve much more severe combustion conditions, including both elevated pressures and large flame runup distances, which result in high turbulence, high flame speeds, and pressure piling (*71*). Thus, safe gap values tend to be much smaller than the ignition quenching distances that involve combustion at low flame propagation rates.

Generation of *static electricity* is commonly known to occur by triboelectrification, i.e., from the frictional action of two electrically unlike materials. The materials can be liquids, solids, and/or gases, one of which needs to be a relatively poor conductor for the charge to accumulate. This frequently occurs in the pumping of fluids, pneumatic transport of solids, and processes involving plastics. Even a human body can accumulate hazardous static charges (*101*). For example, by equation 24, an average human with a capacitance of 300×10^{-12} F and charge of 10,000 V could conceivably produce a static discharge of 0.015 J (15 mJ), which is much greater than the MIE of most combustible-air systems. The ability of a nonconductor (or conductor) to accumulate a static charge will depend upon its resistivity $\frac{(\text{resistance} \times \text{area})}{(\text{length})}$ as well as that of the surrounding medium. Obviously, charge dissipation will be greater in a liquid than in a dry gaseous medium, indicating the importance of humidity.

Thermal Ignition

Most thermal sources other than sparks or arcs tend to be much less localized spatially and temporally. These are discussed below, together with the concept of an ignition temperature or critical heating, which is basic to thermal ignition theory.

1. *Hot Surfaces.*—In the simplest terms, thermal ignition is a combustion reaction in which the limiting condition is determined primarily by the rate of chemical heat release versus the rate of heat loss to the surroundings. The rate of chemical heat release (q_1) by the Semenov theory (*93*), which assumes a uniform temperature distribution, is given by

$$q_1 = VQZ\, a^n e^{-E/RT}, \tag{26}$$

where V is vessel volume, Q is heat reaction, Z is rate frequency factor, a is reactant concentration, n is order of reaction, E is activation energy, R is universal gas constant, and T is the reactant absolute temperature. Also, the rate of heat loss (q_2) is defined by

$$q_2 = \alpha S (T - T_o), \tag{27}$$

where α is heat transfer coefficient, S is wall surface area, and T_o is wall temperature. The critical heating condition for ignition is that temperature and pressure at which $q_1 = q_2$. Based on this theory, ignition temperature will be a function of the S/V ratio of the vessel, or roughly its reciprocal diameter ($S/V \propto d^2/d^3 = 1/d$). The variation of the *time delay to ignition* (τ) with temperature is given by the following useful expression:

$$\tau P^n = A\, e^{E/RT}, \tag{28}$$

which at constant pressure (P) yields

$$\log \tau = \frac{0.22\,E}{T} + A', \tag{29}$$

where A and A′ are system constants and E is the apparent activation energy of the global processes controlling τ, i.e., the temperature coefficient of ignition delay. The lowest temperature that can accelerate the reaction to ignition occurs when the ignition delay (or induction period) is maximized and the vessel S/V ratio is minimized; this temperature is commonly referred to as the *minimum autoignition temperature* (AIT).

Figure 5 illustrates typical AIT data obtained for the n-decane-air system by injecting various quantities of liquid fuel in an open heated vessel; a plot of log τ versus 1/T is more useful to define E and A in equation 29. Corresponding data under flowing conditions, where the contact time with the heated surface is shorter (<1 s), would be characterized by smaller τ and greater AIT values. In all such ignitions, the AIT's will be sensitive to fuel composition, fuel-oxygen ratio, pressure, and nature of the container surface. Generally, hot surface ignition temperatures increase with decreasing diameter or area of the heat source, although this dependence may not be uniform over a wide temperature range.

2. *Self-heating.*—A more rigorous thermal theory is one developed by Frank-Kamenetskii (*21*, p. 209) in which a nonuniform temperature distribution is assumed. It is particularly suitable for predicting the size of the reactant mass that may undergo self-heating at various ambient temperatures. Here, time delay to ignition can be of the order of hours or days in the case of adiabatic self-heating, as opposed to only minutes or seconds in the case of isothermal heating by an external source. The *self-heating*

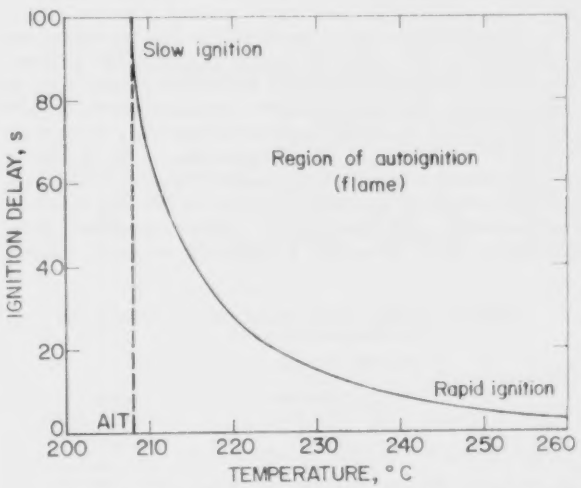

Figure 5.—Ignition delay versus temperature for autoignition of n-decane in air at atmospheric pressure.

rate (q) is defined as the sum of the chemical heat release rate (q_1) and the conductive heat loss rate (q_2):

$$\underset{(q)}{\rho C \frac{\partial T}{\partial t}} = \underset{(q_1)}{\rho Q Z e^{-E/RT}} + \underset{(q_2)}{\lambda \nabla^2 T} \qquad (30)$$

where ρ is density, C is specific heat, λ is thermal conductivity, ∇^2 is a differential operator, and other quantities have the same meaning as above. For steady state conditions ($\partial T/\partial t = 0$), $q_1 = q_2$ and the critical mass radius (r_c) that will self-heat is

$$r_c = \left[\frac{\delta_c \lambda RT^2}{\rho E Q Z e^{-E/RT}}\right]^{1/2}, \qquad (31)$$

where δ_c is a shape factor that is equal to 3.33 for a sphere, 2.0 for a cylinder, and 0.88 for plane-parallel slabs. For adiabatic conditions ($\partial T/\partial x = 0$), $q = q_1$ and the critical temperature rise rate for self-heating is

$$dT/dt = \frac{QZ}{C} e^{-E/RT} \qquad (32)$$

Thus, autoignition by self-heating is strongly dependent upon the dimensions of the reactant mass, whereas autoignition by external heating depends more upon the dimensions of the heat source (heated vessels, wires, rods, etc.). In real self-heating situations, convective heat transport cannot be fully neglected as done in equation 30. For example, the self-heating of conical coal piles is due in part to the favorable "chimney effect" that can occur during the weathering of coal; furthermore, the *heat of wetting* itself can be greater than the heat of oxidation at ambient temperature. In all ignitions of combustible solids, the reactions will be particularly sensitive to particle size, bed porosity, moisture conditions, and the air ventilation rate.

3. *Hot Gases.*—As with heated surfaces, ignitions by hot gas sources also differ in their temporal and spatial characteristics. *Shock wave heating* (nonisentropic) is the most localized in space and time (e.g., <1 ms), whereas *adiabatic compression heating* (isentropic) is more spatially distributed and, therefore, should effect ignitions of combustible mixtures at lower temperatures. Table 5 compares the air temperatures possible in shock wave and adiabatic compression heating at various pressure ratios; it is apparent that shock compression temperatures are noticeably greater than adiabatic compression temperatures at a given pressure ratio. According to this table, it would appear that a combustible-air mixture with an AIT of 200° C could be ignited at a shock pressure ratio of at least 5 or an adiabatic compression ratio of 10. However, in both cases, much higher pressure ratios would be required because of the short duration of heating involved (milliseconds) as opposed to those associated with minimum AIT's (minutes). Essentially, ignition will not occur unless the elevated heating conditions are maintained for a duration that exceeds the ignition delay at the given temperature.

Table 5. — Shock wave and adiabatic compression temperatures of air (*66*, p. 516)

(P_1 = 14.7 psia; T_1 = 0° C)

Compression ratio (P_2/P_1)	Gas compression temperature (T_2)	
	Shock wave °C	Adiabatic compression °C
2	62	57
5	208	152
10	432	242
50	1,988	521
100	3,588	677
1,000	18,840	1,435

Other hot gas ignitions can involve *heated jets* of air, inert gas, or gaseous combustion products, including luminous and nonluminous flames. They are intermediate on the temporal and spatial scale of heating by hot gases. Although these ignitions involve more complex heat and mass transport processes than in hot surface ignitions, they are also a thermal type and depend upon the enthalpy or heat flux of the heat source. The heat flux of the hot gas jet will depend upon its temperature, diameter, velocity, and composition. Reported ignition temperatures by hot gas jets tend to be higher than those by hot surfaces, but the differences are not likely to be great when compared at the same heat source diameter and fuel contact time with the heat source.

4. *Thermal Radiation.*—Ignitions under this category include those in which a combustible is raised to its AIT by exposure to the thermal radiation of a hot gas, hot surface, or other infrared heat sources, including a fire. Solid or condensed combustibles have the greatest capacity to absorb radiative heating and, therefore, are most likely to be ignited by this heating mode. The radiative ignition requirements for any combustible are usually defined in terms of a critical heat flux. For ordinary combustible solids, the critical *radiant heat flux* for ignition can be a relatively small value (1 to 2 cal/(cm^2·s)), depending upon the ignition temperature of the solid. Such critical radiation intensities can be easily encountered when the combustible is exposed to a nearby flame source since the maximum radiation intensity can be 10 to 30 cal/(cm^2·s) near the flame surface. Generally, approximately 15 to 40 pct of the theoretical thermal output of a large flame source will be radiated to the surroundings (*7*). Assuming spherical geometry and a flame point source, the radiant heat flux (h_x) at various distances (x) from a flame source, such as a burning pool of radius r, can be estimated by

$$h_x = \frac{h_r \pi r^2}{4 \pi x^2}, \qquad (33)$$

where h_r is the maximum radiative heat flux at the flame surface. The assumption of a hemispherical pool fire model will yield twice the irradiances predicted by equation 33. Factors that can determine the level of thermal flame radiation include fuel-oxidant stoichiometry, soot formation (fuel-rich hydrocarbon flames), and radiative properties of the gaseous combustion products. Hydrogen flames are typical of a low-radiative emitter, and benzene flames, which tend to produce considerable soot, are representative of a high-radiative emitter.

Chemical Ignition

This category represents a special case of autoignition in which the heat of chemical reaction alone can produce ignition at or below ambient temperature. One type is a *pyrophoric reaction* where the combustible ignites spontaneously upon mere exposure to air, as in the self-reaction of alkali metals, metal alkyls, or metal hydrides. Such reactions are usually promoted by the presence of moisture and can involve the formation and ignition of a flammable gas; the combustibles in this case are also referred to as water-reactive substances.

Another type is a *hypergolic reaction* where spontaneous ignition occurs when a combustible is intimately mixed

with a highly reactive oxidizer. These ignitions can occur with ordinary and high-energy fuels and particularly with such high-strength oxidizers as fluorine, hydrogen peroxide, nitrogen tetroxide, and concentrated acids. Their heats of reaction can be calculated from available heats of formation. In the case of acid-base systems, heats of neutralization are typically about 13 to 14 kcal/mol for a strong acid and strong base in aqueous solution. If one also considers the heats of solution, the total heat release can be about 25 to 35 kcal/mol and sufficient to initiate a combustion reaction.

Chemical ignitions also result from *catalytic reactions*. The most common catalysts in organic reactions are finely divided metals, but many different substances can serve as catalysts, depending upon the chemical reactants. Contaminants that accumulate on the walls of a reaction vessel may serve as either ignition catalysts or inhibitors.

FLAME PROPAGATION PROCESSES

Flammable Mixtures

A flammable gaseous mixture of combustible and oxidant is one that, when ignited, will propagate flame beyond the influence of the ignition source. All combustible gases and combustible vapors of liquids or solids form flammable mixtures over a limited range of combustible concentrations, depending upon temperature, pressure, and nature of the oxidant. The critical combustible concentrations are known as the *limits of flammability* or explosion limits of the system and are defined as the fuel-lean or *lower limit* (L) and the fuel-rich or *upper limit* (U). These limits are usually in volume percent and refer to homogeneous combustible vapor-oxidant mixtures. Since the flammability limits vary with temperature and since the vapor formation of a combustible in its liquid or solid state is strongly dependent on temperature, it is useful to construct a flammability concentration-temperature diagram of the type shown in figure 6. A three-dimensional plot to include the pressure effect would be required to completely define the flammability domains.

As shown in figure 6, the flammable mixtures of a combustible liquid-air system may consist of mists (droplets + saturated vapor + air), saturated vapor-air mixtures (vapor pressure curve), or neat vapor-air mixtures (region beyond saturated vapor temperatures). The temperature range over which the liquid can form flammable vapor concentrations is defined by its *temperature limits* of flammability (T_L and T_U); intersections of these temperature limits with the vapor pressure curve define the *concentration limits* of flammability (L and U) at liquid-vapor equilibrium conditions. At higher temperatures, flammability domains for the neat vapor-air mixtures become widened, particularly on the fuel-rich side. Eventually, the temperature can be sufficient to produce autoignition of the mixtures, as illustrated in figure 6.

The lower temperature limit (T_L) is of great practical interest because it defines the minimum temperature to which a combustible liquid or solid must be heated to form a flammable vapor-air mixture, i.e., the lower limit of flammability (L). In practice, this temperature corresponds approximately to the *flashpoint* of the combustible, which is determined under less ideal conditions (downward flame propagation and nonuniform mixtures) than those used in flammability limit determinations (upward propagation and uniform mixtures). *Closed cup flashpoints* are the most reliable values. It is evident from figure 6 that flammable mists, sprays, or foams can form below the flashpoint or T_L of the combustible. However, their ignition energy requirements are much more severe than for neat vapor-air mixtures. The flammability characteristics of mists can be expected to approximate their vapor behavior when the droplet size of the mist is less than about 10 μm.

Various flammability diagrams are used to present complete limit of flammability data for combustible vapor-oxidant-inert systems (*110*). Most data are presented in the form of a rectangular plot, as in figure 7 for the aviation gasoline vapor-air-nitrogen system (*42*). In this plot, the flammability limits in the oxidant alone (air) are found on the ordinate (1.3 and 7.1 pct combustible); also, the variations of these limits with added inert (N_2) are indicated

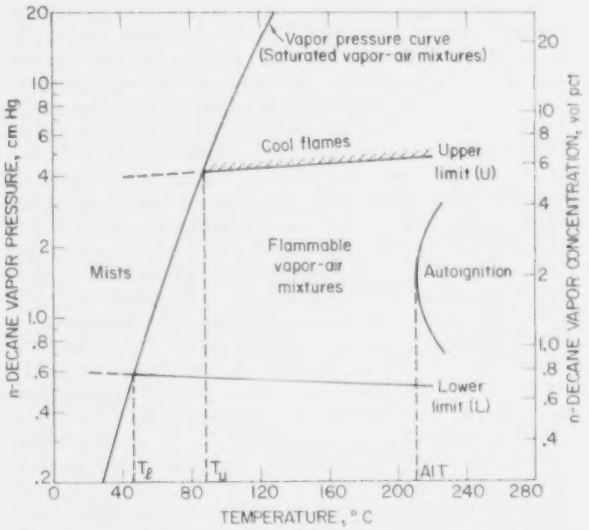

Figure 6.—Flammability and vapor pressure diagram for n-decane vapor-air system at various temperatures and atmospheric pressure.

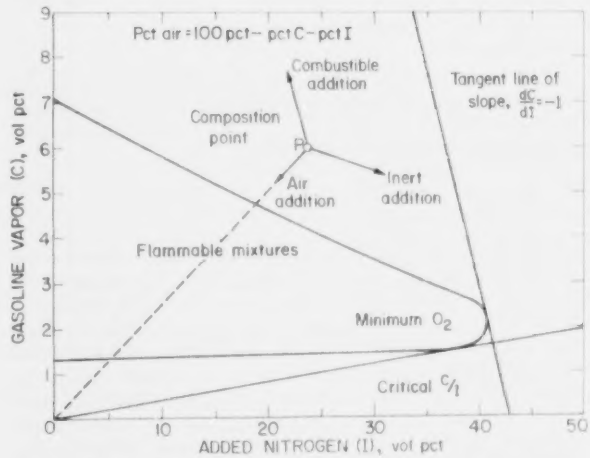

Figure 7.—Flammability diagram for the aviation gasoline vapor (100/130 grade)-air-nitrogen system at 25° C and 1 atm.

by the lower and upper boundaries defining the complete range of possible flammable mixtures for the total system. Any mixture composition point is defined by the following relation:

$$\text{Pct oxidant (air)} = 100 \text{ pct} - \text{pct combustible (C)} - \text{pct inert (I)} \quad (34)$$

The variation of a composition by the addition or reduction of any mixture component is illustrated for a composition (P) outside the flammable zone. Note that additions of air to this composition point could result in the formation of flammable mixtures (see dashed line), but that additions of combustible or inert could not form mixtures that fall into the flammable zone.

Also of great practical interest are the *minimum oxygen concentration* (minimum O_2) and critical *combustible-inert ratio* (critical C/I) below which flammable mixtures cannot form. The minimum O_2 is obtained by drawing a constant oxidant tangent line of negative slope ($dC/dI = -1$) to the nose of the flammability diagram, whereas the critical C/I is found by constructing a tangent line from the origin to the lean side of the nose of the curve. The former is important in determining inerting requirements, and the latter in assessing fire extinguishing requirements.

Generally, limits of flammability are widened by increased temperature, pressure, oxygen concentration, and energy of the ignition source. The limits are also widened by turbulence and buoyancy effects, which increase the flame propagation rate. Essentially, flammability limits may be classified according to their propagation mode, upward or downward. *Upward limits* have the greatest practical value because they include the buoyancy effect and reflect the maximum flammability hazard; *downward limits* exclude buoyancy and are of greater fundamental significance. In addition to buoyancy, the differences between molecular diffusivities of the combustible and oxidant can contribute to the wide variations often observed between these limits; recent papers by Burgess (*5*) and Hertzberg (*30*) provide in-depth discussions of the relevant processes of "selective diffusional demixing" and buoyancy. As with ignition limits, flammability limits are narrowed by heat losses to vessel walls, and propagations can become impossible at some *quenching diameter*.

Prediction of Limits

If the flammability limits of the components of a mixture are known, the limits of the mixture may be calculated by *Le Chatelier's law* (*65*). The specific form of this law for lower limits of complex mixtures in air is

$$L = \frac{100}{C_1/L_1 + C_2/L_2 + \cdots C_i/L_i}, \quad (35)$$

where C_1, C_2---C_i are the proportions of each combustible gas in the mixture, free from air, L_1, L_2---L_i are the lower limits of each combustible gas in air, and L is the lower limit of the complex mixture in volume percent. Although this law predicts fairly reliable lower limits for mixtures of many common fuel gases, it tends to be less reliable for upper-limit calculations because of the more complex reactions. Also, its application to limits of upward propagation that are greatly influenced by preferential diffusion (H_2-air) and to limits of materials that involve chemical flame inhibition (extinguishing agents) presents uncertainties (*5*). The application of Le Chatelier's law to mixtures that include various added inerts is much more complicated and is given in a comprehensive treatment by Coward (*11*).

One of the most useful expressions for predicting the variation of lower flammability limits with temperature is a modified Burgess-Wheeler law suggested by Zabetakis (*110*) for combustible-air mixtures:

$$L_T/L_{25} = 1 - \frac{0.75}{L_{25}\Delta H_c}(T - 25°), \quad (36)$$

where L_T and L_{25} are the lower limits (vol pct) at temperatures T(° C) and 25° C, ΔH_c is net heat of combustion (kcal/mol), and 0.75 is essentially a molar heat capacity constant × 100. If the combustion heat release $\left(\frac{L_{25}\Delta H_c}{100}\right)$ can be assumed to be a constant value, as it is for many hydrocarbons, the lower limits of the combustibles should decrease linearly with increasing temperature and converge at some limit temperature which corresponds to zero concentration ($L_T = 0$). For hydrocarbons, this limit temperature is about 1,300° C. (See "Flame Temperatures," below). Equation 36 can also be used to calculate the ideal flashpoint of a combustible if its L_{25} value and vapor pressure-temperature relationship are known; construction of a flammability diagram such as figure 6 facilitates this determination. A similar expression is also proposed for upper limits that increase drastically with temperature. However, these calculated values are not always reliable because of cool flames, soot formation, or other incomplete combustion modes associated with fuel-rich flames.

Flame Temperatures

Flames are formed when the gaseous reaction products are heated above some critical temperature that can produce luminous combustion. Those formed by homogeneous gaseous mixtures are defined as *premixed flames* and have well-defined flame temperatures and propagation rates. The maximum flame temperature, $(T_f)_M$, of a mixture is found under adiabatic conditions at or near stoichiometric fuel-oxidant concentrations. In comparison, the *limit flame temperature*, $(T_f)_L$, is the minimum temperature at which a normal flame can be sustained and is, therefore, the value for a lower limit mixture. A simple expression for estimating the flame temperature of a lower limit mixture (L, volume percent) in air under constant pressure is given by

$$(T_f)_L = T_i + \Delta T = T_i + \frac{L\Delta H_c}{100\,\overline{C}_p}, \quad (37)$$

where T_i is ambient temperature, ΔT is temperature rise, ΔH_c is heat of combustion, and $\overline{C}_p$ is average molar heat capacity of the gaseous products between T and the flame temperature $(T_f)_L$. Note that this equation can be derived from Zabetakis' equation 36 by substituting $100\,\overline{C}_p$ for the 0.75 constant and letting L_T/L_{25} equal zero. A general procedure for obtaining reliable estimates of flame temperatures for combustible-oxidant-diluent systems is outlined below.

For the lower limit mixture of methane (5 pct) in air at 25° C (298 K), the reaction for complete combustion of 1 mol (n) of mixture may be written as

$$0.05\ CH_4 + 0.20\ O_2 + 0.75\ N_2 \rightarrow 0.05\ CO_2 + 0.10\ H_2O(g) + 0.10\ O_2 + 0.75\ N_2. \quad (38)$$

The heat of reaction (combustion) is defined from standard heats of formation (ΔH_f) at 298 K as

$$\Delta H_{298} = \Sigma n \Delta H_f \text{ (products)} - \Sigma n \Delta H_f \text{ (reactants)} \quad (39)$$

where ΔH_{298} is the heat release per mol of reactant (kcal/mol). The approximate temperature rise of the product gases for constant pressure combustion is

$$\Delta T(\text{products}) = \frac{\Delta H_{298}}{\Sigma n\, Cp(\text{products})} \cong \frac{\Delta H_{298}}{\overline{C}_p(\text{mixture})} \quad (40)$$

where

$$\overline{C}_p\,(\text{mixture}) = 0.05\ \overline{C}_p\,(CO_2) + 0.10\ \overline{C}_p\,(H_2O) + 0.10\ \overline{C}_p\,(O_2) + 0.75\ \overline{C}_p\,(N_2). \quad (41)$$

The heat content (H) data in table 3 can be used to determine the average heat capacity values $\frac{(H_2 - H_1)}{(T_2 - T_1)}$ that will satisfy equation 40 at the assumed T_2 flame temperature. Since the lower limit combustion enthalpy (ΔH_{298}) of many C-H-O-N combustibles is 10 to 11 kcal per mol of mixture and $\overline{C}_p$ of their products is about 8×10^{-3} kcal/(mol·K), their limit flame temperature can be assumed to be close to 1,300° C. Noticeable deviations from this generalization occur for combustible systems of very high or very low reactivity. Rigorous solutions are necessary for precise flame temperature calculations (*24*, p. 283; *66*, p. 590).

The temperature rise for constant volume combustion is given by

$$\Delta T(\text{products}) \cong \frac{\Delta E_{298}}{\overline{C}_v(\text{mixture})} = \frac{\Delta H_{298} - \Delta n RT_1}{\overline{C}_v(\text{mixture})} \quad (42)$$

where ΔE_{298} is constant volume heat release, Δn is molar change of gaseous reactants and products, and $\overline{C}_v = \overline{C}_p - R$. These temperature rises tend to be at least 20 pct higher than those found under constant pressure.

Another category of flaming combustion is *diffusion flames*, which are encountered in most fires, such as burning of a liquid pool, solid surface, or flared fuel gas. These heterogeneous flames have a wide spectrum of combustible concentrations and, therefore, do not have definitive flame temperatures or flammability limits, per se. Flames of dispersed dusts also involve diffusional and heterogeneous burning. However, if they are uniformly mixed in air, their flames can have some of the fundamental properties of premixed flames even though they may be less well defined. No simple theory is available for predicting dust flame temperatures, but the values for carbonaceous dusts are roughly equivalent to those of the hydrocarbon vapors that can form as a result of heating of the dust.

Cool flames are also a special category of combustion and are usually associated with low-temperature oxidations and two-stage ignitions. They are formed by many hydrocarbons including ethers, aldehydes, alcohols, and paraffins. These flames are ordinarily pale blue and are believed to result from aldehyde and/or peroxide formation. They are most often found with fuel-rich mixtures that are outside the normal flammability domain of the fuel vapor-air system. Because only a small fraction of the available enthalpy is used to form cool flames, their temperatures are very low, typically of the order of a few hundred degrees Celsius. They cannot be ignored because they may produce normal ignitions if brought into contact with flammable vapor-oxidant compositions.

Burning Velocities

The linear rate at which a laminar combustion wave (reaction zone) propagates relative to the unburned gas of a flammable mixture is the *burning velocity* (S_u). This velocity is a fundamental property of the mixture and depends primarily upon the thermal diffusivity $\frac{(\lambda)}{(\rho C_p)}$, chemical reaction rate, and heat of combustion. Although the mechanism of flame propagation is very complex, it is well known that certain physical processes can quench propagation and account for the existence of a limit burning velocity and corresponding limit of flammability. For example, if only natural convection and buoyancy effects are considered, the *limit burning velocity*, $(S_u)_L$, for a lower limit mixture can be predicted with reasonable accuracy by the equation proposed by Hertzberg (*30*):

$$(S_u)_L = (2\ \alpha\ g\ \rho_b/\rho_u)^{1/3}, \quad (43)$$

where g is gravitational constant, α is thermal diffusivity, and ρ_b/ρ_u is density ratio of burned and unburned gas. This equation defines the horizontal propagation limit where the buoyancy force just balances the combustion force of the product gases and predicts $(S_u)_L$ values to be less than 10 cm/s for a variety of fuel-air mixtures.

Of great practical interest is the *flame speed* (S_f) associated with combustion, i.e., the flame velocity sensed by an observer. It may be defined as

$$S_f = S_u + S_g, \quad (44)$$

where S_g is a gas velocity component associated with the expansion and buoyancy of the product gases. Figure 8, which was obtained by Andrews (*3*), illustrates the expected relationship between S_u, S_f, and S_g for spherical CH_4-air

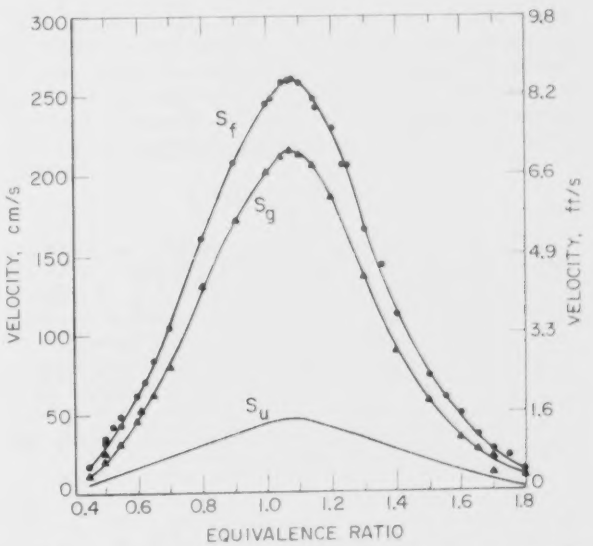

Figure 8.—Flame speed (S_f), gas velocity (S_g), and burning velocity (S_u) versus equivalence ratio for methane-air flame propagation at 25 C and 1 atm.

propagations as a function of equivalence ratio (fraction of stoichiometric). Note that maximum S_f and S_u values occur on the rich side of stoichiometric and their ratio (S_f/S_u) is about 6. Under adiabatic conditions, the maximum S_f/S_u ratio is closer to approximately 7.5, which is typical of the combustion product *expansion ratio* (E) for most combustibles. Thus, the flame speed may be calculated from the following expressions:

$$S_f = S_u E \tag{45}$$

$$S_f = S_u \, \rho_u/\rho_b = S_u \frac{M_u T_b P_u}{M_b T_u P_b} \tag{46}$$

where the u and b subscripts refer to the unburned and burned states, respectively. The burning velocity itself generally increases consistently with increasing initial temperature, whereas the pressure effect is usually positive in oxygen but negative in air for many combustibles. In oxygen, burning velocities are considerably greater because of increased reaction rates and heats of reaction, particularly at stoichiometric combustible concentrations, which are much higher in oxygen than in air.

The foregoing discussion is applicable primarily to laminar flame propagation of mixtures initially at rest. With the mixtures under dynamic conditions, S_u can be expected to vary with the degree of turbulence and S_f will increase from the combined effects of turbulence and any added flow. If the propagations occur in a long tube or duct, the flames can accelerate and may even develop into detonations (see next section), depending upon the length-diameter ratio. Since turbulent flames involve severe velocity gradients and distorted flame fronts, they are not amenable to simple generalizations like laminar flames.

In the case of burning liquid pools, the burning rate (regression rate) is a strong function of the pool diameter because of the radiation feedback effect. With increased heat feedback, the rates of vaporization and reaction are enhanced. Zabetakis (*111*) has shown that the burning rate for large pools (v_∞, cm/min) is given by

$$v_\infty = k_v \, \Delta H_c/\Delta H_v, \tag{47}$$

where ΔH_c is net heat of combustion, ΔH_v is sensible heat of vaporization, and k_v is a constant that is 0.0076 for hydrocarbon fuels.

EXPLOSION PROCESSES

Deflagrations

The term "explosion" is best defined as a sudden release of pressure or energy. One of the most common types is the deflagration of a flammable mixture which is characterized by subsonic propagation rates relative to the unburned gas. The *explosion pressure* (P_2) of a deflagration is greatest in adiabatic combustion under total confinement, i.e., constant volume. By applying equation 42 to calculate the temperature rise (ΔT), the pressure rise ratio ($P_b/P_u = P_2/P_1$) for constant-volume adiabatic combustion of a mixture can be obtained from

$$P_2/P_1 = \frac{n_2 T_2}{n_1 T_1}, \tag{48}$$

This equation predicts that the maximum P_2/P_1 ratio for the confined deflagration of most combustible-air systems is about 8:1 to 9:1.

Assuming ideal propagation after central ignition in a spherical enclosure, the pressure rise (ΔP) may be estimated from the expression suggested by Zabetakis (*110*):

$$\Delta P = K \, P_1 \, S_u^3 \, t^3/V, \tag{49}$$

where t is time, V is enclosure volume, and K is a constant that includes an expansion term and is obtained from an evaluation of the P-V data. Actual pressure rises are less than those predictable by equation 49 because flame propagation rarely is uniformly spherical, heat losses increase with proximity of the flame front to the vessel walls, and S_u is not constant nor maximum throughout constant-volume combustion. Nevertheless, this equation is fairly reliable for rapid-burning mixtures, such as stoichiometric mixtures, which can readily form spherical flames and are least affected by wall and buoyancy effects. Figure 9 (*47*) illustrates the pressure history for the deflagration of a stoichiometric CH_4-air mixture in the Bureau's large spherical vessel (3.65-m diam); here, an S_u of 45 cm/s is appropriate for determining the K factor applicable in equation 49. In such spherical explosions, where propagation is near ideal, the time to reach maximum pressure (P_2) is approximated by the following expression:

$$t_2 = \frac{\text{vessel radius}}{S_f} = \frac{\text{vessel radius}}{E \, S_u} \tag{50}$$

where the E and S_u values for constant-pressure combustion may be used.

Explosion pressures of mixtures less optimum than stoichiometric are generally lower because of decreased enthalpy and burning velocity, but also because of the restricted mode of flame propagation—upward, horizontal, or downward. As shown by Sapko (*92*), the spatial mode of propagation varies greatly with mixture composition and is strongly related to buoyancy effects. Figure 10 shows the flame and pressure histories obtained in the Bureau's large vessel for a partly inerted CH_4-air-N_2 mixture (upward and only slight downward propagation) and a near-limit

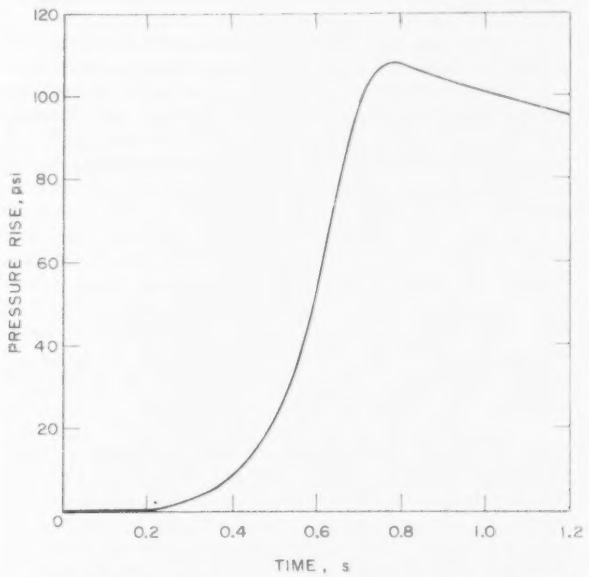

Figure 9.—Pressure history for the explosion of a stoichiometric methane-air mixture in a 3.65-m (12-ft) diam sphere at 25° C and 1 atm.

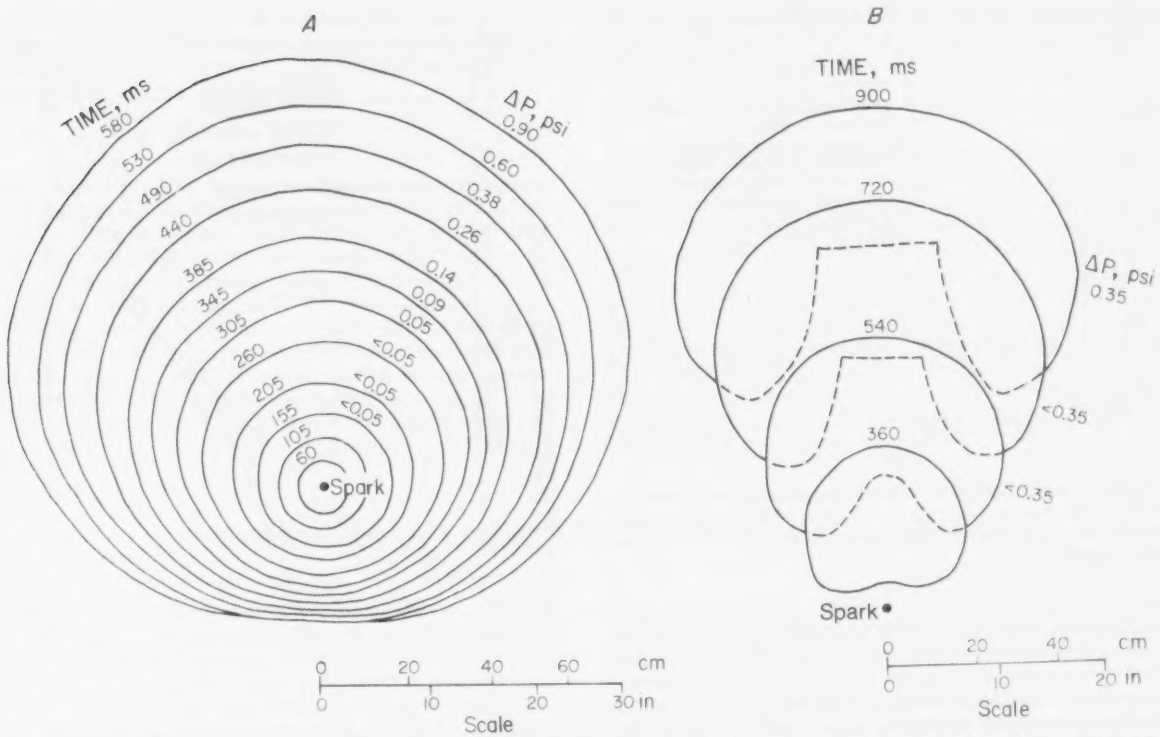

Figure 10.—Pressure and flame profile histories for spark ignitions of (*A*) 7.8 pct CH_4-74.1 pct air-18.1 pct N_2 mixture and (*B*) 6.9 pct CH_4-65.8 pct air-27.3 pct N_2 mixture in a 3.65-m (12-ft) diam sphere at 25° C and 1 atm.

CH_4-air-N_2 mixture (only upward propagation). Buoyant velocities of the highly inerted flames will vary roughly with the square root of the fire ball radius, which is predicted by theory for rising gas bubbles.

The maximum work output or energy release of a combustible explosion is given by equation 12 or 13, depending upon whether an isothermal or adiabatic condition is assumed. Since neither condition is fully attained in real situations, the actual energy release will fall somewhere between the values for the two possible cases.

Physical Explosions

Many explosions are the physical type in which no combustion takes place. These would include outward burstings of confined gas systems due to overpressurization by mere physical processes; inward burstings (implosions) due to insufficient pressurization are also a physical type. The potential energy release associated with such physical eruptions may be treated simply as the thermodynamic expansion or compression of an inert gas. Some explosions involve a combination of physical and chemical energy release, such as in a boiling liquid-expanding vapor explosion, which culminates in a large fireball. Liquefied petroleum gases are normally involved in these explosions and result when the fuel container is excessively heated by an external fire and ruptures from overpressurization. The fireball diameter may be estimated by the following expression (*32*):

$$d = 3.86\ W^{0.32}, \qquad (51)$$

where d is fireball diameter (m) and W is fuel weight (kg).

Detonations

The most severe type of explosion is a detonation that is characterized by supersonic propagation rates relative to the unburned reactant. Detonations are commonly associated with liquid or solid explosives but can also occur with many gaseous fuel-oxidant systems under certain initiation or propagation conditions. Detonations are unique in that their combustion wave is coupled to a shock wave which results in very high pressures under either confined or unconfined conditions. The *detonation pressure* (P_2) for gaseous mixtures can be estimated by the following expression:

$$P_2 = 2\ P_v \qquad (52)$$

where P_v is the maximum pressure for constant-volume combustion (equation 48). Thus, the maximum pressure rise ratio (P_2/P_1) for gaseous detonations is about 18:1, depending upon the energy of the mixture.

Figure 11 by Burgess (*6*) is typical of the pressure history that can result in a well-developed gaseous detonation; these data are for a stoichiometric acetylene-air mixture in a 45.7-m-long tunnel (0.61-m diam) with one end open. Three pressure levels are worth noting here: C–the initial spike (Von Neumann) or shock front, which is of very short duration with an insignificant impulse ($\int Pdt$); D–the well-defined Chapman-Juguet (C-J) pressure, which corresponds to complete combustion within the detonation front but which also produces little impulse; and E–the static pressure, which reflects the expansion of gas and beyond which the pressure remains at a plateau until relieved.

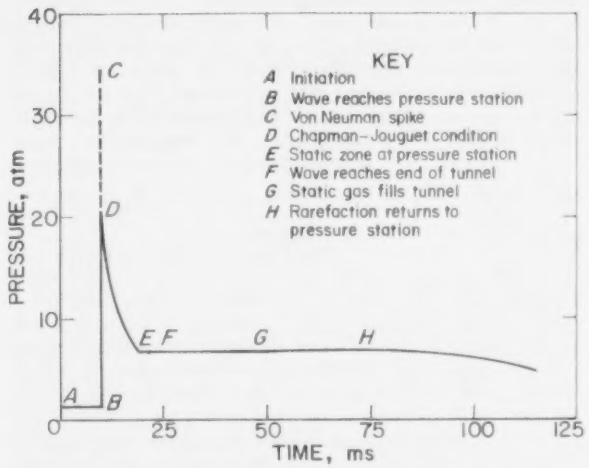

Figure 11.—Pressure-time transient for detonation of a stoichiometric acetylene-air mixture in a 45.7-m (150-ft) long tunnel with initiation end closed. Instrument station 18.3 m (60-ft) from initiator point.

The pressure at the C-J condition is the detonation pressure (P_2) referred to in equation 52. In comparison, the reflected pressure is often about 2.5 times the C-J detonation pressure. Although detonation pressures are of great concern, it is the static pressures (E-H plateau) of the expanded gases that produce the greatest pressure energy because of their much greater duration and impulse; this is fully realized in a closed system.

Many more rigorous expressions than equation 52 are available for calculating detonation parameters. The following expression (*106*) relates the pressure rise ratio (P_2/P_1) across the C-J detonation front with the *detonation velocity* (v^*):

$$P_2/P_1 = \frac{1 + \gamma_1(v^*/c_1)^2}{1 + \gamma_2}, \qquad (53)$$

where γ_1 is ratio of specific heats (C_p/C_v) and c_1 is sonic velocity $(\gamma_1 RT_1)^{1/2}$ of the reacting gas; γ_2 refers to the molecular and dissociated products and varies somewhat with any shifting product composition. Although precise γ_2 values require elaborate thermochemical computations, they may be roughly estimated from specific heat tables for any assumed reaction products and their adiabatic flame temperatures; the latter temperature is usually a few hundred degrees less than the detonation temperature. The term v^*/c_1 is the *Mach number* (M) of the detonation wave, which theoretically propagates at a constant velocity as it moves through the unreacted gas, usually several times the sonic velocity of the unburned gas. For most practical applications, the estimation of P_2 by equation 52 is sufficiently reliable and adequate.

Any strong explosion that discharges into the free atmosphere, as in a detonation or deflagration failure of an enclosure, propagates for some distance as an *air blast wave*, which is characterized as an air shock wave ($M \geq 1$). Blast waves associated with detonations propagate over much greater distances and at greater velocities than those of deflagrations. The damage potential of an air blast wave can be characterized by its overpressure (ΔP_s), which is

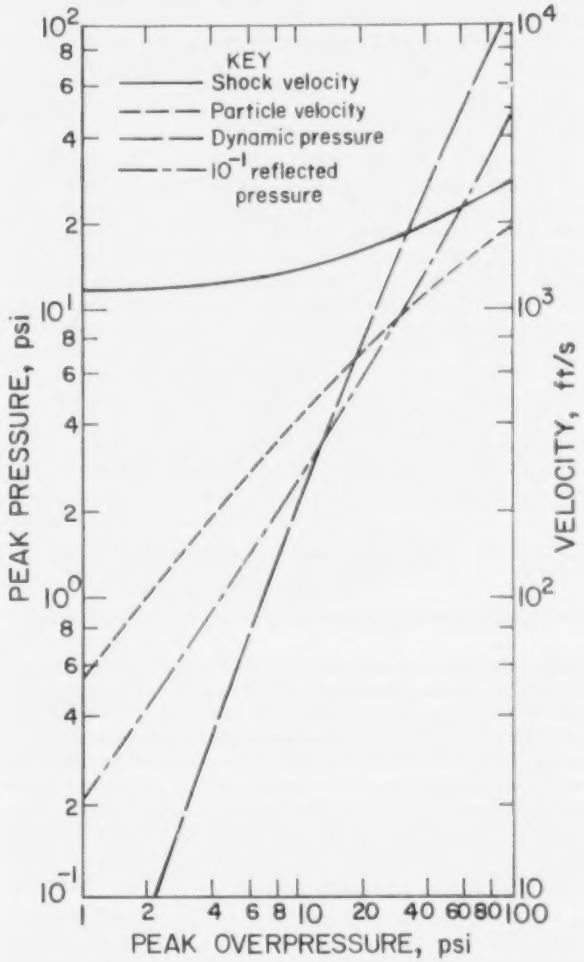

Figure 12.—Relation of ideal blast wave characteristics at the shock front to peak overpressure.

the static or side-on shock pressure (P_s) minus the ambient pressure (P_o). By air shock theory (26),

$$\Delta P_s = P_o \frac{2\gamma(M_o^2 - 1)}{\gamma - 1}, \qquad (54)$$

where γ is the specific heat ratio of air (~ 1.4) and M_o is the ratio of the shock wave velocity (v_s) to the sonic velocity of air (v_s/c_o); c_o is 331 m/s at 0° C. The total pressure that is sensed by an object exposed to a shock wave is the sum of the static shock pressure (ΔP_s) and the dynamic pressure ($1/2\ \rho v^2$) associated with the wind velocity (particle velocity, v). Figure 12 (*26*, p. 123) shows the normal relationship of such pressure and velocity parameters for an ideal air blast wave. Note that the dynamic pressure is negligible for weak shocks but becomes equal to the peak static overpressure of a strong shock at approximately 70 psi.

The blast wave pressure at various distances from the explosion source should be proportional to the cube root of the explosion energy yield if the chemical energy conversion to pressure energy is ideal, as in the case of TNT and other high explosives. The *TNT equivalence* of a strong

explosion can be computed by invoking the cube root scaling law (*26*, p. 127) that relates the blast pressure potential to the exploding charge weight (W) and distance (d) from the exploding charge, relative to TNT:

$$d/d_o = (W/W_o)^{1/3}, \quad (55)$$

where d_o and W_o refer to TNT. It is convenient to express W_o in terms of unit TNT mass, such as 1 ton or 1 gram, which is defined to yield about 10^9 cal/ton or 1,100 cal/g (*101*); thus $d = d_o W^{1/3}$ for a unit mass of TNT ($W_o = 1$). Corresponding blast pressures can then be compared in terms of a scaled distance ($d/W^{1/3}$).

TNT equivalents of solid and liquid explosives can be reliably estimated from their calculated heats of detonation and the value for TNT. However, in the case of gaseous explosions, the fraction of available chemical energy (ΔH_c) that is converted into blast energy or pressure energy can vary greatly with the degree of confinement and ability of the gas mixture to detonate (*6*). Assuming adiabatic expansion, the work that can be converted into blast pressure energy is given approximately by

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}, \quad (56)$$

where P_2 is elevated pressure of the gaseous products and P_1 is ambient pressure of the gases after expansion. In weakly confined gaseous deflagrations where the container walls fail before the maximum potential combustion pressure is achieved, P_2 will be small and little of the chemical energy (<10 pct) will result in blast pressure energy. In strongly confined deflagrations in which the containment fails, a small fraction of the chemical energy (~10 pct) will be used to cause wall failure, and the pressure energy will be slightly less than ΔH_c. The TNT equivalent for such strong gaseous deflagrations, as well as gaseous detonations, can be assumed to approximate the ΔH_c of the mixture for constant-volume combustion.

PROPERTIES OF LIQUID AND GASEOUS COMPOUNDS

This section covers selected combustion properties of a great number of liquid and gaseous organic compounds, as well as some common inorganic fuels. Pertinent physical properties of the combustibles and their flashpoints, autoignition temperatures, and flammability limits in air are given in the summary tabulations in appendix A. The data are grouped according to the chemical class of combustible to make apparent the effects of chemical structure within a homologous series and between chemical families of combustibles. These data are summarized in the text and supplemented with other data of interest for evaluating ignitability and flammability hazards.

VAPOR PRESSURES AND FLASHPOINTS

Since the flashpoint of a combustible liquid or solid depends upon its volatility and the vapor concentration required to form a lower limit of flammability in air, vapor pressure-temperature curves are important in assessing the flammability hazard. Accordingly, vapor pressure curves and flashpoint data are presented herein for selected combustibles of each chemical class of compounds. Flashpoints obtained by closed cup methods, which best approximate the lower temperature flammability limit (T_L), are reported here provided such data were available. Any reported open cup values may be assumed less conservative, particularly if the vapor concentration indicated by the flashpoint is appreciably higher than the lower limit (L) obtained from limit-of-flammability experiments.

Saturated Hydrocarbons

Vapor pressure curves and flashpoint data are given in figures 13 and 14 for the straight-chain paraffins and in figure 15 for branched-chain paraffins; the vapor pressures are predominantly from Stull (*99*) and the flashpoints from Bureau, NFPA, and other references cited in appendix A. Corresponding vapor concentrations, assuming 1 atm total pressure (76 cm Hg), are also included in the figures to permit estimation of lower flammability limits from the flashpoints. According to these data, normal alkanes with more than eight carbon atoms (above octane) will not form flammable vapor-air mixtures below 30° C and atmospheric pressure; also chain branching increases the volatility and decreases the flashpoint, as evident in comparing the values for n-octane (14° C) and 2,2,4-trimethylpentane or isooctane (−12° C). Generally, flashpoints of a paraffin series increase with increasing molecular weight, whereas the corresponding vapor pressures and lower flammability limits vary inversely.

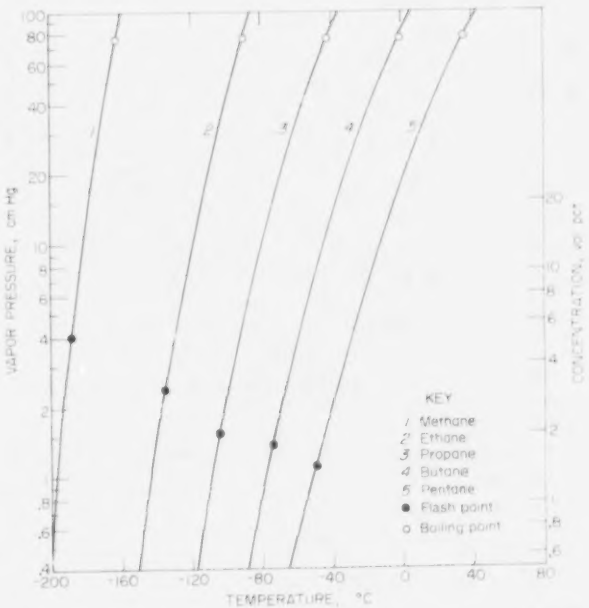

Figure 13.—Vapor pressure-temperature curves and flashpoints for five normal paraffins (C_1 to C_5).

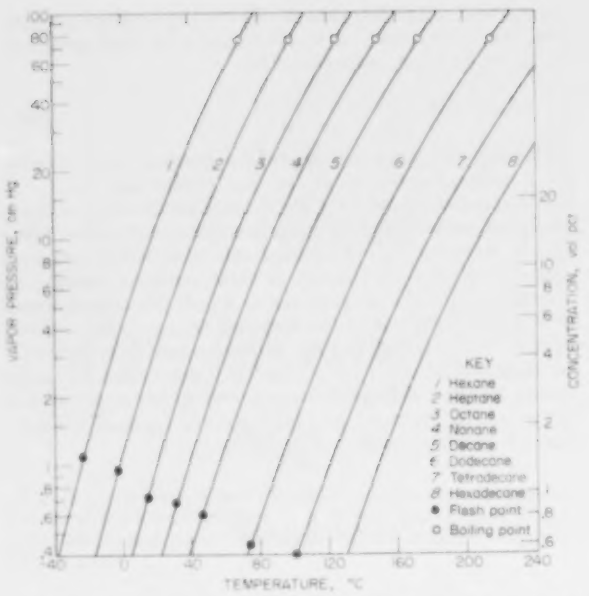

Figure 14.—Vapor pressure-temperature curves and flashpoints for eight normal paraffins (C_6 to C_{10}, C_{12}, C_{14}, C_{16}).

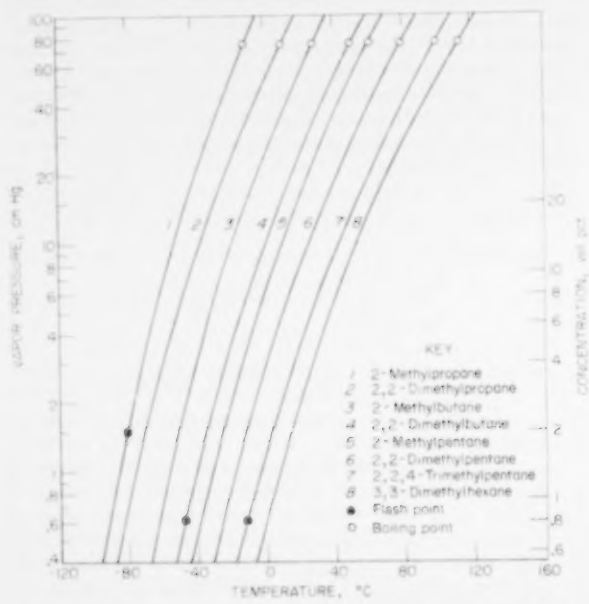

Figure 15.—Vapor pressure-temperature curves and flashpoints for eight branched-chain paraffins.

Based on similar data, Affens (*1*) has derived the following expressions for predicting the flashpoints (T_F, ° C) of the normal paraffins:

$$(T_F + 277.3)^2 = 10{,}410\ n, \tag{57}$$

$$(T_F + 277.3)^2 = 741.7/P_F, \tag{58}$$

and

$$(T_F + 277.3)^2 = 77{,}291\ (1/L_{25}) - 3{,}365, \tag{59}$$

where n is number of carbon atoms, P_F is vapor pressure (atm) at T_F, and L_{25} is the lower flammability limit (vol pct) in air at 25° C. Agreement between calculated and literature values is good except for methane. Additional correlations of this type can be made by substituting known relationships between number of carbon atoms and molecular weights, boiling points, or heats of combustion. The method proposed by Zabetakis (*110*) is equally reliable and is based upon equation 36, which predicts lower limits of mixtures as a function of their calorific values ($L_{25}\Delta H_c$) and temperature. This method also requires vapor pressure data but is attractive in that either actual calorific values or an assumed constant may be used in calculating the flashpoint.

Other Combustibles

Vapor pressure curves and flashpoint data for other families of combustibles are presented in figures 16-32. As with the paraffins, the flashpoints of each homologous series generally increase with increasing number of carbon atoms and decrease with chain branching. Ellis (*17*) finds the correlations with carbon atoms and heats of combustion to be practically linear for certain normal alkyl compounds (paraffins, cyclohexanes, ketones, alcohols, acetates) and alkyl benzenes but not for their isomers. The addition of functional groups can have a large and varied effect on flash point as illustrated below:

For butane:	°C	For benzene:	°C
C_4H_{10}	−74	C_6H_{10}	−11
$C_4H_9NH_2$	−12	C_6H_5Cl	29
C_4H_9Cl	−9	C_6H_5Br	51
C_3H_7CHO	−7	$C_6H_4Cl_2$	66
C_4H_9SH	2	$C_6H_5NH_2$	70
C_4H_9Br	18	C_6H_5OH	79
C_4H_9OH	29	$C_6H_5NO_2$	88
C_3H_7COOH	72		

The effects of any functional group on the flashpoint will depend upon the changes produced in both volatility and the lower flammability limit. As a rule, the flashpoints of such hydrocarbon derivatives will be noticeably greater than those of their parent hydrocarbons.

For blends of any combustible liquids, flashpoint predictions are more complex and will depend upon their deviations from ideal mixture laws (equations 4 and 5) and Le Chatelier's mixture flammability law (equation 35). Anomalous behavior is most likely to occur with dissimilar molecular species, such as mixtures of a hydrocarbon and a halogenated, oxygenated, or nitrated hydrocarbon. Ellis (*17*) has shown that the flashpoints of many solvent blends are often lower than expected because of polarity, hydrogen bonding, or solubility parameter differences. In practice, the greatest concern is necessarily for the liquid mixture component of highest volatility. Where a highly volatile component is present in only small concentrations as an additive or contaminant, the flashpoint will be subject to the evaporative history of the mixture. Depending upon the evaporation period, the actual flashpoint hazard may be underestimated when the volatile additive is nonflammable and overestimated when the additive is more flammable than the main liquid components. Such uncertainties are often encountered in evaluating cleaning solutions, paint mixtures, water-based lubricants, and modified fuels or chemicals. In the case of controversy, their flashpoints should be confirmed by limit-of-flammability-type experiments.

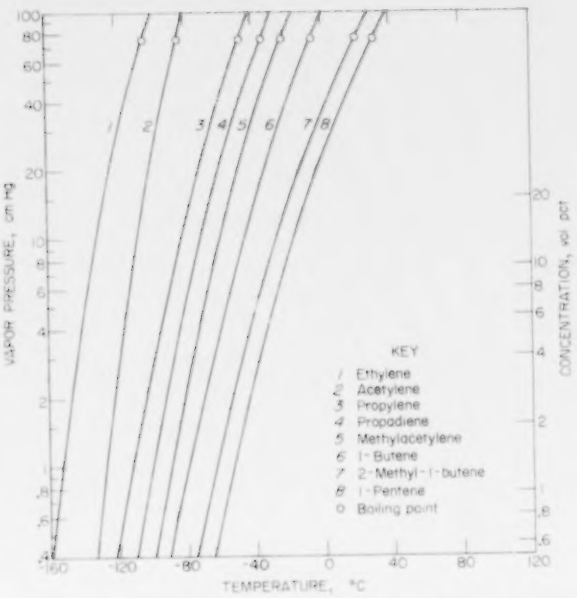

Figure 16.—Vapor pressure-temperature curves for eight unsaturated hydrocarbons.

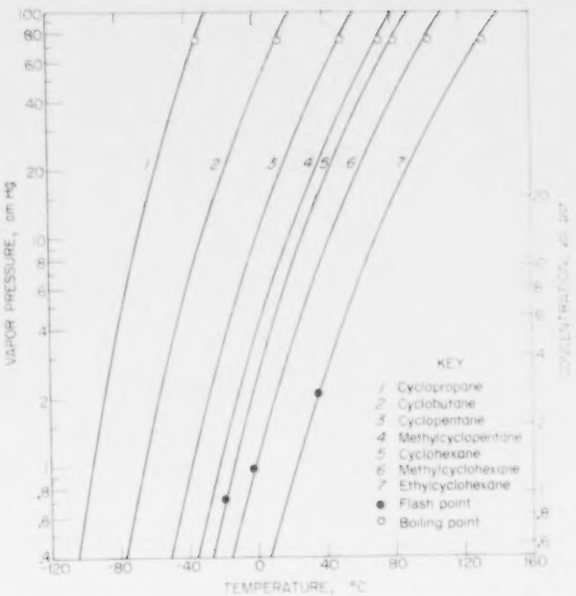

Figure 17.—Vapor pressure-temperature curves and flash-points for seven alicyclic hydrocarbons.

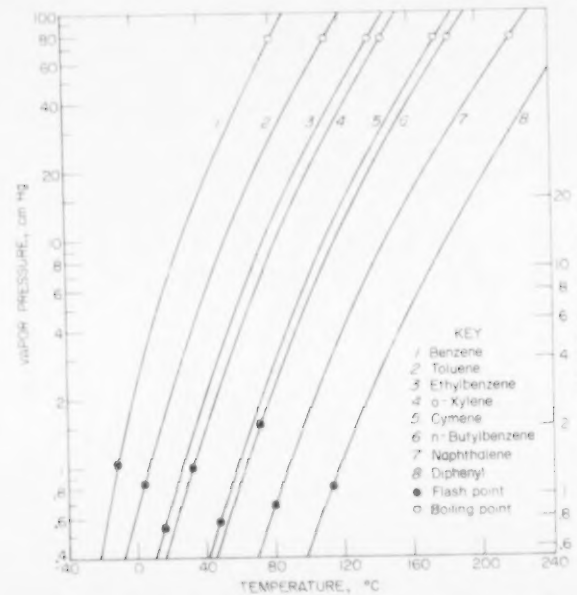

Figure 18.—Vapor pressure-temperature curves and flash-points for eight aromatic hydrocarbons.

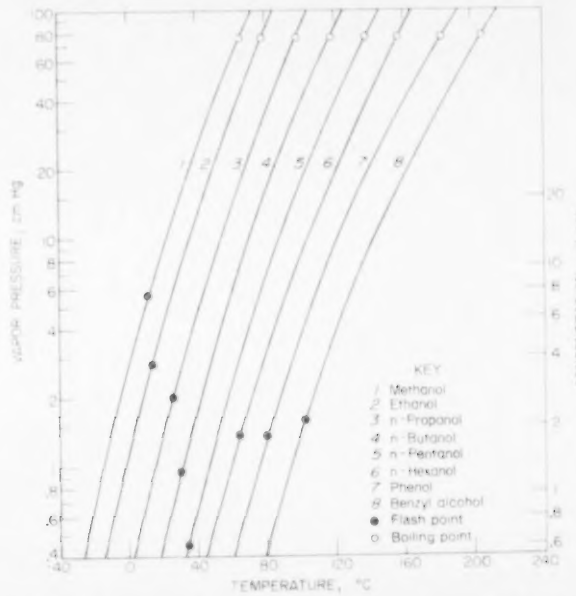

Figure 19.—Vapor pressure-temperature curves and flash-points for eight alcohols or hydroxy compounds.

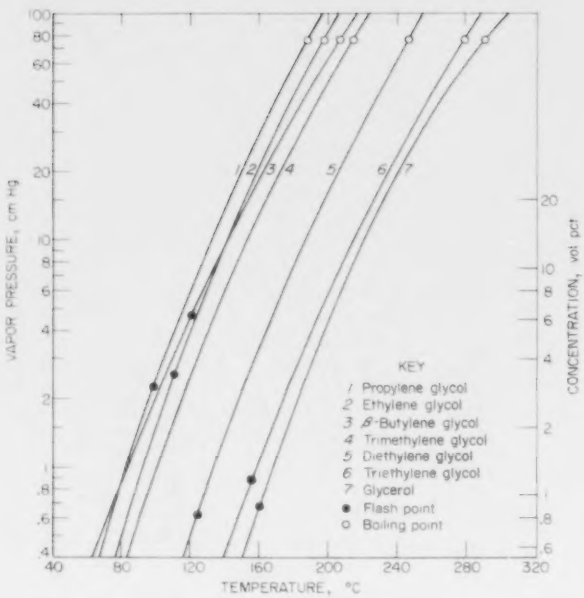

Figure 20.—Vapor pressure-temperature curves and flash-points for six glycols and glycerol.

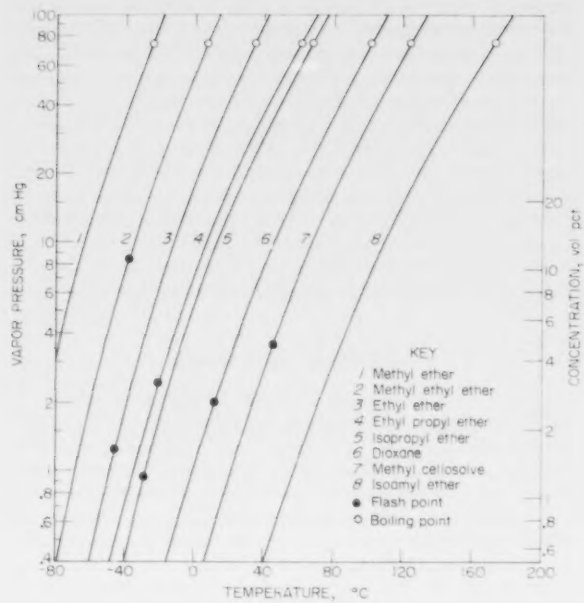

Figure 21.—Vapor pressure-temperature curves and flash-points for eight ethers.

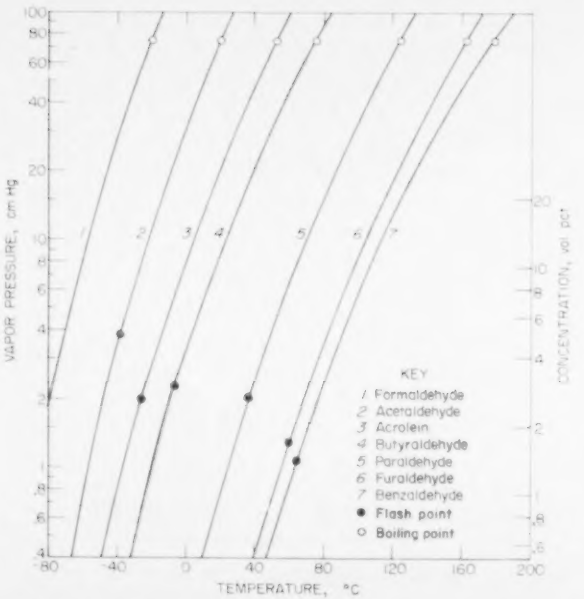

Figure 22.—Vapor pressure-temperature curves and flash-points for seven aldehydes.

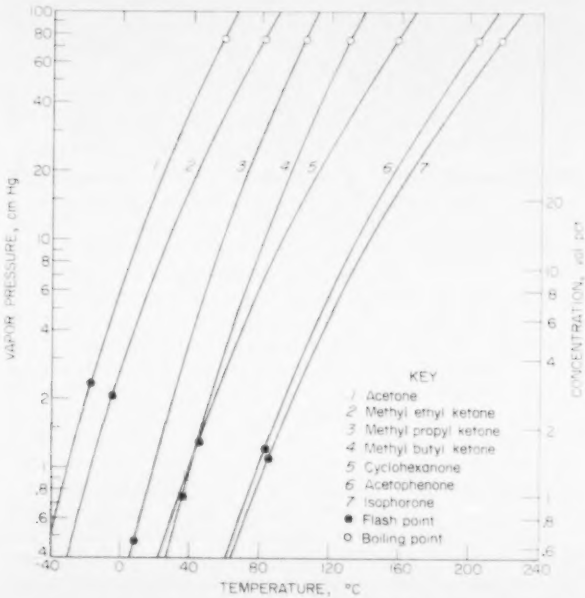

Figure 23.—Vapor pressure-temperature curves and flash-points for seven ketones.

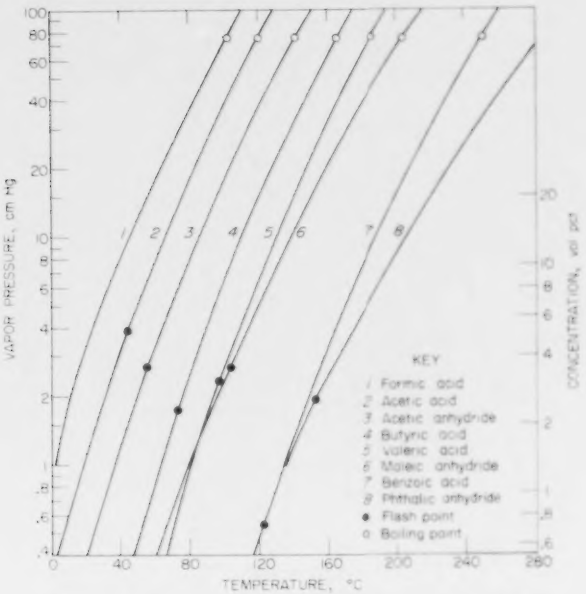

Figure 24.—Vapor pressure-temperature curves and flash-points for five acids and three acid anhydrides.

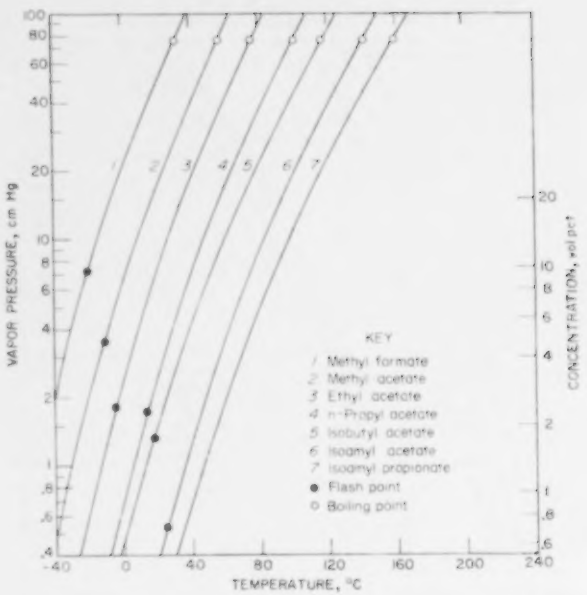

Figure 25.—Vapor pressure-temperature curves and flash-points for seven esters.

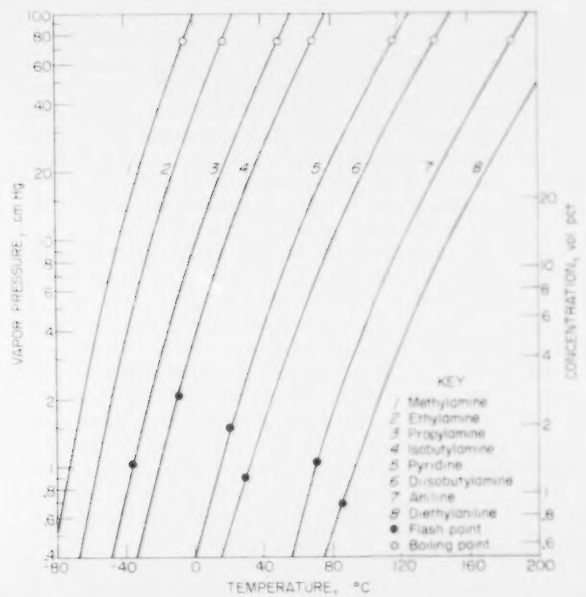

Figure 26.—Vapor pressure-temperature curves and flash-points for eight amines.

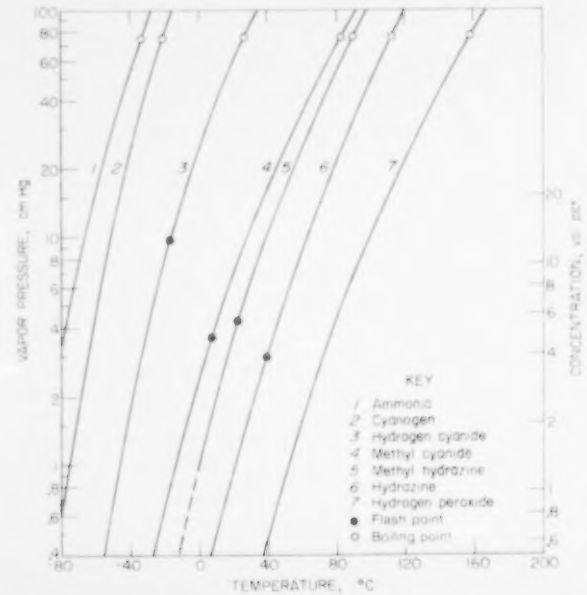

Figure 27.—Vapor pressure-temperature curves and flash-points for ammonia, cyanogen, two cyanides, two hydrazines, and hydrogen peroxide.

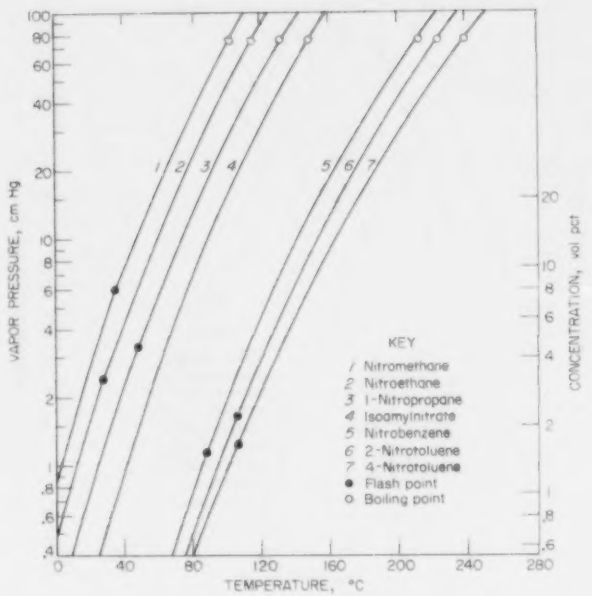

Figure 28.—Vapor pressure-temperature curves and flash-points for seven nitrated hydrocarbons.

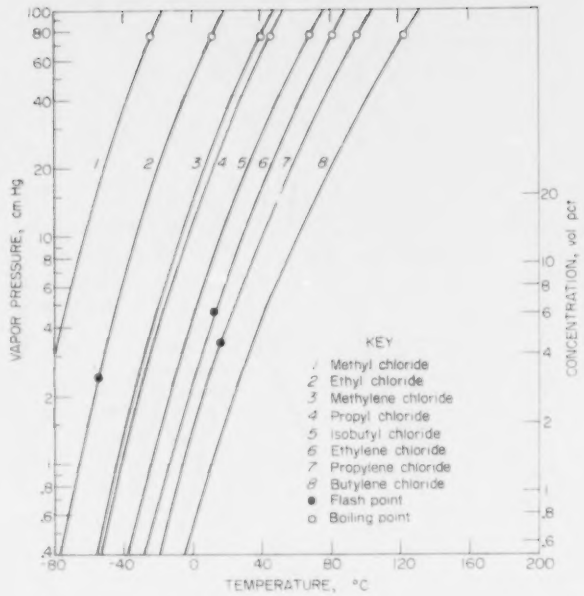

Figure 29.—Vapor pressure-temperature curves and flash-points for eight alkyl chlorides.

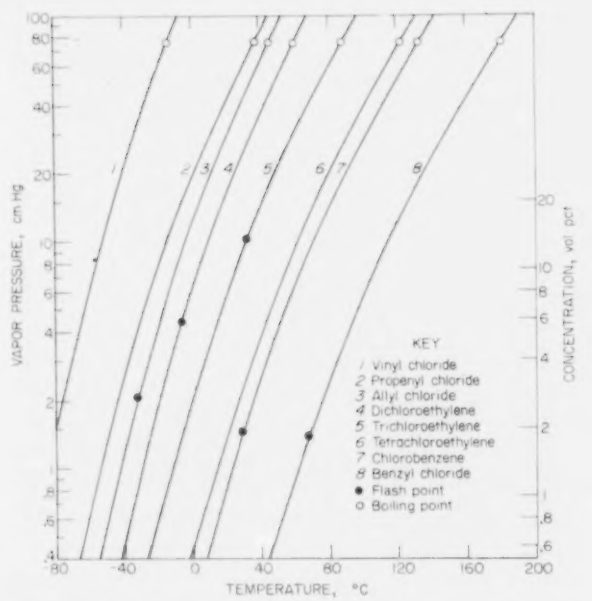

Figure 30.—Vapor pressure-temperature curves and flash-points for six unsaturated and two aromatic chlorine compounds.

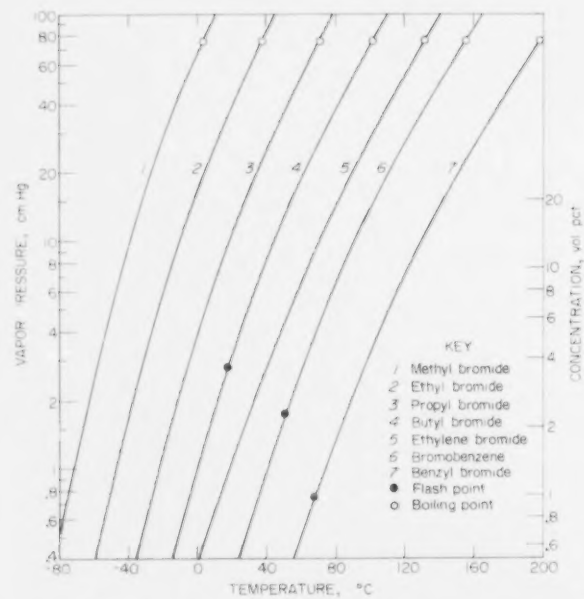

Figure 31.—Vapor pressure-temperature curves and flash-points for seven brominated compounds.

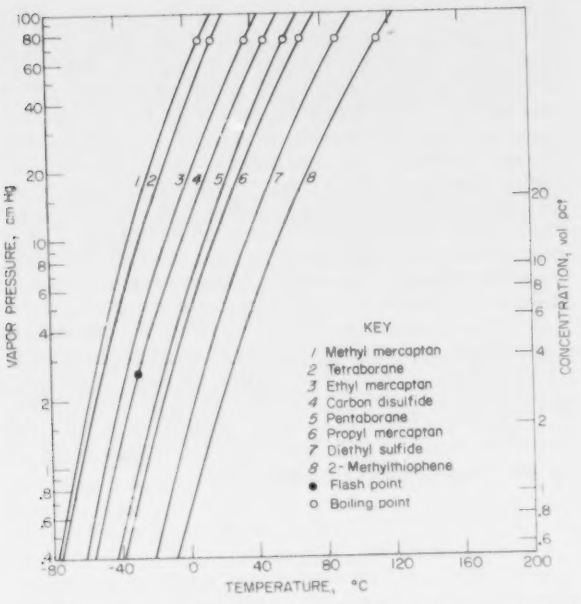

Figure 32.—Vapor pressure-temperature curves and flash-points for six sulfur and two boron compounds.

FLAMMABILITY LIMITS IN AIR AND OXYGEN

Lower limits (L_{25}) and upper limits (U_{25}) of flammability of individual gases or vapors in air are systematically tabulated in appendix A for the members of many families of combustibles. These limits define the range of flammable vapor-air concentrations for ignitions of quiescent uniform mixtures at atmospheric pressure and 25° ± 5° C and with propagation in the *upward* optimum mode; some data are given at temperatures higher than 25° C, mostly because of vapor pressure limitations. Unless otherwise specified, these data and those presented in the text were taken largely from compilations of earlier Bureau bulletins (*11*, *110*) and other cited Bureau publications; most Bureau flammability limit determinations were made in cylindrical tubes of at least 5-cm diameter with an electrical spark ignition source, as described in reference 117. Any data uncertainties because of possible inadequate ignition energies or apparatus dimensions (wall effects) would be greatest for combustibles having large ignition energies and quenching distances, such as the halogenated hydrocarbons. Typically, the reported limits have a precision of ± 0.1 at 1 vol pct and ± 0.5 at 10 vol pct, which is adequate for most safety applications. Thus, previously accepted data were not rejected because of subtle differences observed in later studies.

Limits of flammability in oxygen or other oxidizers are much less complete than those in air for most families of combustibles. A comparison of limit data in air and oxygen is made in table 6 for a number of hydrocarbons, halogenated hydrocarbons, and other combustibles at atmospheric pressure and 25° C (or the indicated temperature). The range of flammable concentrations for each combustible is considerably greater in oxygen than in air, except for acetylene, which can propagate flame even in the absence of air. The increased hazard with oxygen is reflected primarily by the great increase of upper limits of flammability (U_{25}). Although lower limits (L_{25}) in oxygen should be equal to or less than those in air, some of the reported data are inconsistent in this respect; this is not totally unexpected since all data were not obtained from a single source or by the same apparatus. The flammability limits in such oxidants as chlorine and nitrogen tetroxide also tend to be wider than in air, although these data are meager (*54*, *110*). Flammability trends of the different classes of combustibles are briefly summarized in the next sections.

Table 6. — Limits of flammability of combustible vapors in air and oxygen at 25° C and 1 atm[1]

Combustible	Flammability limits, vol pct			
	Air		Oxygen	
	L_{25}	U_{25}	L_{25}	U_{25}
HYDROCARBONS				
Methane	5.0	15.0	5.0	61
Ethane	3.0	12.4	3.0	66
Propane	2.1	9.5	2.3	55
n-Butane	1.8	8.4	1.8	49
n-Hexane	1.2	7.4	1.2	[2]52
n-Heptane	1.1	6.7	.9	[2]47
Acetylene	2.5	100	≤2.5	100
Ethylene	2.7	36	2.9	80
Propylene	2.4	11	2.1	53
α-Butylene	1.6	10	1.8	58
Cyclopropane	2.4	10.4	2.5	60
Benzene	[2]1.3	[2]7.9	≤1.3	NA
HALOGENATED HYDROCARBONS				
Methyl chloride	10.7	17.4	~8.0	~66
Ethyl chloride	3.8	15.4	4.0	67
n-Butyl chloride	1.8	[2]10	1.8	[2]52
Methylene chloride	[2]15.9	[2]19.1	13.6	[2]68
Ethylene chloride	6.0	[2]17.3	5.6	[2]68
Methyl chloroform	6.8	NA	6.6	[2]57
Trichloroethylene	[3]12.0	[2]41	7.5	[2]91
Vinyl chloride	3.6	33	4.0	70
Isocrotyl chloride	2.9	9.3	4.2	[4]66
Ethyl bromide	6.7	11.3	6.7	44
Isocrotyl bromide	6.4	12	6.4	[4]50
OTHER COMBUSTIBLES				
Acetaldehyde	4.0	60	4.0	93
Acetone	2.6	13	≤2.6	[2]60
Ammonia	15.0	28	15	79
Carbon monoxide	12.5	74	≤12.5	94
Ethyl ether	1.9	36	2.0	[4]82
Hydrogen	4.0	75	4.0	94
Isopropyl ether	1.4	7.9	≤1.4	[4]69
Methanol	6.7	[5]36	≤6.7	[4]93
Vinyl ether	1.7	27	≤1.7	[4]85

NA Not available.
[1]Based upon data in references 11, 54, 78, and 110.
[2]Data at 100° C.
[3]Data at 30° C.
[4]Temperature unknown but >25° C.
[5]Data at 60° C.

Saturated Hydrocarbons and Derivatives

The lowest member of the paraffin series is methane, which has a lower limit of 5 pct and an upper limit of 15 pct in normal ambient air. For most homologous series of organic combustibles, their flammability limits in air or oxygen decrease with increasing molecular weight or number of carbon atoms. This is illustrated in figure 33 where lower and upper limits are plotted versus carbon atoms for the vapor-air mixtures of the normal paraffins and their corresponding alcohols, aldehydes, amines, and chlorides; the curves approximate the limits given in table 6 or appendix A at 1 atm and ≥25° C. The indicated limits

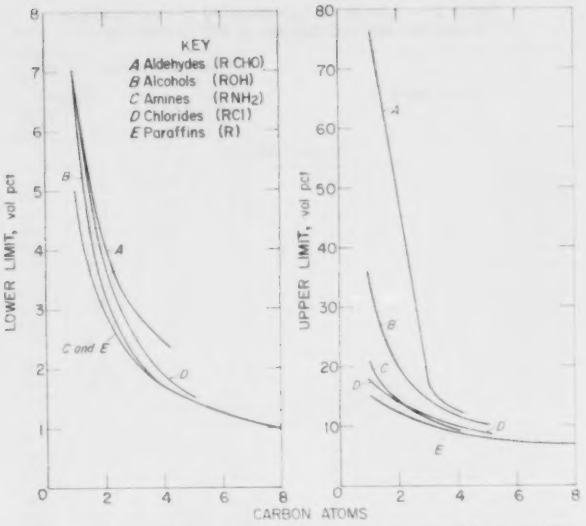

Figure 33.—Variation of lower and upper limits of flammability in air with number of carbon atoms for normal paraffins and their derivatives. Data at 25° C or reported temperature.

for the straight-chain paraffins can be assumed to be practically the same as for their branched-chain isomers and only slightly wider than for their cyclic homologs.

In comparison, many other paraffin derivatives have a wider range of flammability than their parent hydrocarbons, particularly because of large differences between their upper limits. Such derivatives include the primary or simple aldehydes, alcohols, and ethers, many of which form cool flames readily and have substantially wider limits than their corresponding paraffins; primary amines and certain esters (formates), which have a flammability range roughly comparable to that of the ethers; alkyl nitrates, nitrites, and hydrazines, which may undergo highly exothermic decomposition with or without air; and the alkyl mercaptans. Other derivatives such as the primary acids and simple ketones have flammability limits comparable to or slightly wider than those of the normal paraffins, whereas those of the halogenated homologs are narrower or wider, depending upon the number of carbon and halogen atoms. As a rule, the effect of a monosubstituted group tends to be minimum at a carbon chain length of about four or more; for example, compare the limits of n-butane (C_4H_{10}) and n-butyl chloride (C_4H_9Cl) in table 6.

The lower limit (L_{25}, volume percent) of paraffin combustibles in air may be approximately predicted by the expression suggested by Lloyd (*70*):

$$L_{25} \cong 0.55\ C_{st}, \qquad (60)$$

where C_{st} is the volume percent for stoichiometric combustion to CO_2 and H_2O. Limit equivalence ratios (L_{25}/C_{st}) given in table 7 show that this equation is fairly reliable for the normal paraffins (n-alkanes), as well as for many of their isomeric, cyclic, and substituted derivatives. However, most aldehydes, alkane bromides, alkane dichlorides, and nitroalkanes have L_{25}/C_{st} values that are much lower or higher than those for paraffins; C_{st} values for all the combustibles are included in appendix A for calculating

Table 7. — Equivalence ratios (L_{25}/C_{st}) and calorific values ($L_{25}\Delta H_c/100$) of lower limit mixtures of saturated hydrocarbons and derivatives in air at 25° C and 1 atm

Formula	L_{25}, vol pct	L_{25}/C_{st}	$L_{25}\Delta H_c/100$, kcal/mol
n-ALKANES (PARAFFINS)			
CH_4	5.0	0.53	9.6
C_2H_6	3.0	.53	10.2
C_3H_8	2.1	.52	10.3
C_4H_{10}	1.8	.58	11.4
C_5H_{12}	1.4	.55	10.9
C_6H_{14}	1.2	.56	11.1
C_7H_{16}	1.1	.59	11.8
C_8H_{18}	[1].95	.58	11.6
ISOALKANES			
C_4H_{10}	1.8	0.58	11.4
C_5H_{12}	1.4	.55	10.9
C_8H_{18}	.95	.58	11.6
CYCLOALKANES			
C_3H_6	2.4	0.54	11.2
C_4H_8	1.8	.53	11.1
C_5H_{10}	1.5	.55	11.1
C_6H_{12}	1.3	.57	11.5
C_7H_{14}	1.1	.56	11.4
N-ALKYL ALCOHOLS			
CH_3OH	6.7	0.55	10.7
C_2H_5OH	3.3	.51	10.1
C_3H_7OH	[1]2.2	.49	9.9
C_4H_9OH	[1]1.7	.50	10.1
$C_5H_{11}OH$	[1]1.4	.51	10.4
$C_6H_{13}OH$	[1]1.2	.53	10.7
ALKYL ALDEHYDES			
HCHO	7.0	0.40	8.7
CH_3CHO	4.0	.52	10.6
C_2H_5CHO	2.9	.58	11.9
C_3H_7CHO	2.5	.68	13.9
ALKYL KETONES			
$(CH_3)_2CO$	2.6	0.52	10.5
$(C_2H_5)_2CO$	1.9	.52	10.4
ALKYL ETHERS			
$(CH_3)_2O$	3.4	0.52	10.7
$(C_2H_5)_2O$	1.9	.56	11.5
$(C_4H_9)_2O$	1.5	.87	17.9
$(C_5H_{11})_2O$	.7	.51	10.5
N-ALKYL AMINES			
CH_3NH_2	4.9	0.58	11.4
$C_2H_5NH_2$	3.5	.66	13.3
$C_3H_7NH_2$	2.0	.52	10.5
$C_4H_9NH_2$	1.7	.57	11.4
ALKYL ESTERS			
$HCOOCH_3$	5.0	0.53	10.9
$HCOOC_2H_5$	2.8	.50	10.3
$HCOOC_4H_9$	1.7	.54	11.1
CH_3COOCH_3	3.2	.57	11.5
$CH_3COOC_2H_5$	2.2	.55	11.1
$CH_3COOC_3H_7$	1.8	.58	11.7
$CH_3COOC_4H_9$	[1]1.4	.55	11.0
n-ALKYL HALIDES			
CH_3Cl	7.0	0.56	10.7
C_2H_5Cl	3.8	.58	11.4
C_3H_7Cl	2.6	.59	11.6
C_4H_9Cl	1.8	.53	10.7
CH_3Br	10.0	.82	15.2
C_2H_5Br	6.7	1.03	19.9
C_4H_9Br	[1]2.5	.74	14.8
ALKANE DICHLORIDES			
CH_2Cl_2	[1]15.9	0.92	18.3
$C_2H_4Cl_2$	[1]4.5	.58	11.7
$C_3H_6Cl_2$	3.4	.68	13.7
NITROALKANES			
CH_3NO_2	[1]7.3	0.33	11.9
$C_2H_5NO_2$	3.4	.40	10.5
$C_3H_7NO_2$	[1]2.2	.42	10.0

[1]Limits at elevated temperatures.

other limit equivalence ratios. Corresponding correlations of upper limits with C_{st} values are less consistent or more difficult to quantify. Excluding possible cool flames, the upper limits (U_{25}, volume percent) of normal paraffins obey the following expression given in Bulletin 627 (*110*):

$$U_{25} = 4.8\ C_{st}^{1/2}. \quad (61)$$

The limits of these hydrocarbons in air can also be correlated with the number of carbon atoms per molecule (n) as follows (*1*):

$$1/L_{25} = 0.1347\ n + 0.04353;$$
$$1/U_{25} = 0.01337\ n + 0.05151. \quad (62)$$

For most saturated hydrocarbons, their lower limits on a weight basis are approximately 45 ± 5 mg per liter of air at standard conditions (0° C and 1 atm); upper limits typically fall between 200 and 400 mg/L, excluding methane (*110*).

With increased temperature, the lower limits of saturated hydrocarbon vapor-air mixtures decrease in the manner shown in figure 34 for 10 paraffins (*110*); AIT data are included, as is an updated value for methane (630° C). Limits in this figure are extrapolated from room temperature to 1,300° C, assuming the White concept of a constant limit flame temperature (*107*). Applying the modified Burgess-Wheeler law (equation 36), Zabetakis (*110*) assumed a constant calorific value for both lower and upper limits and obtained the following correlations for predicting temperature effects:

$$L_T/L_{25} = 1 - 0.000721\ (T - 25°) \quad (63)$$

$$U_T/U_{25} = 1 + 0.000721\ (T - 25°) \quad (64)$$

where T refers to elevated temperature in ° C. Equation 63 is fairly reliable for the lower limits of the paraffins and many of their derivatives, although a calorific value ($L_{25}\Delta H_c/100$) closer to 11 kcal/mol would be more representative of the data given in table 7; most inconsistencies with calorific values occur with the aldehyde, bromide, and dichloride derivatives. Upper limit predictions based on ideal $U_{25}\Delta H_c/100$ values (not shown) are more tenuous because of incomplete combustion and possibility of cool flames. Data by Cato (*9*) indicate that the upper limits of paraffins above n-butane can increase by much greater amounts than predictable by equation 64 (fig. 35). This behavior appears likely to occur with low-AIT hydrocarbons or other combustibles highly capable of cool or blue flames. Temperature effects reported by Kuchta (*54*) for the flammability limits of four chlorinated hydrocarbons in air and oxygen are summarized in table 8.

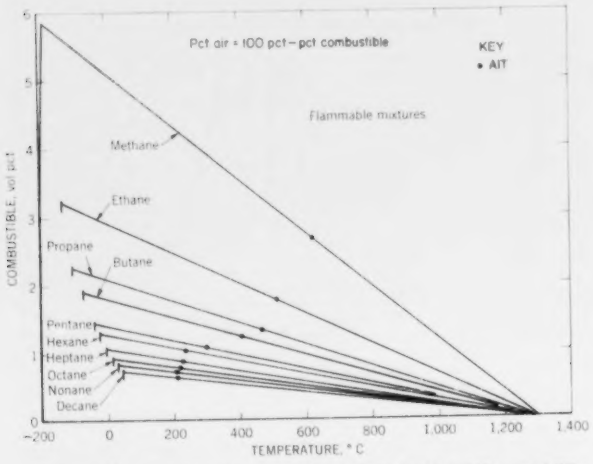

Figure 34.—Temperature effect on lower limits of flammability of 10 normal paraffins in air at atmospheric pressure.

Table 8. — Temperature effects on the flammability limits of four chlorinated paraffins in air and oxygen at 1 atm (*54*)

	Temp, °C	Flammability limits, vol pct			
		Air		Oxygen	
		L_{25}	U_{25}	L_{25}	U_{25}
n-BUTYL CHLORIDE					
(C_4H_9Cl) . . .	25	[1]1.9	8.4	1.8	49
	100	2.0	10.3	1.7	52
	200	1.8	12.0	1.6	56
METHYLENE CHLORIDE					
(CH_2Cl_2) . . .	25	NA	NA	13.6	NA
	100	15.9	19.1	11.7	68
	200	14.9	19.2	11.0	72
ETHYLENE CHLORIDE					
($C_2H_3Cl_2$)	25	6.0	NA	5.6	NA
	100	4.5	17.3	4.0	67.5
	200	3.9	21.2	3.5	69
METHYL CHLOROFORM					
($C_2H_3Cl_3$)	25	[1]6.8	[2]>10.5	6.6	NA
	100	6.3	13.0	5.5	57
	200	5.9	14.3	4.1	60

NA Not available.
[1]Interpolated values from flammability diagrams.
[2]Value limited by vapor pressure of fuel.

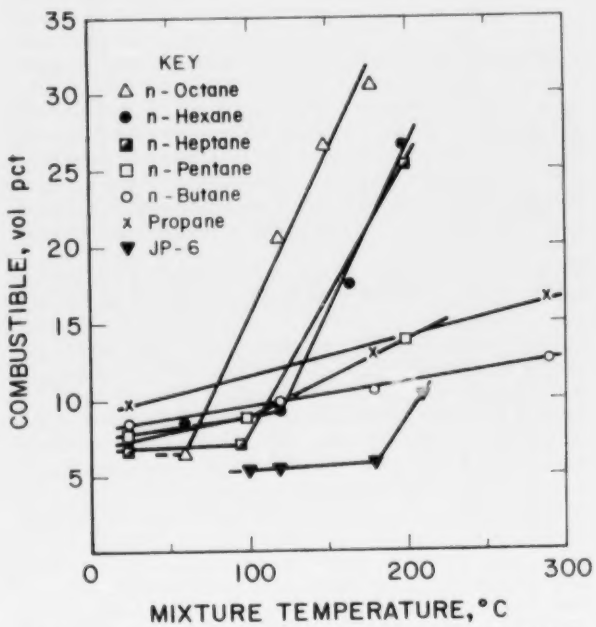

Figure 35.—Temperature effect on upper limits of flammability of six normal paraffins and JP-6 jet fuel in air at atmospheric pressure.

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Flammability limits of hydrocarbon vapor-air mixtures vary only slightly with reduced pressure except at very low pressures, such as below 1/4 atm, where ignition energy or quenching distance becomes the most critical factor. Thus, limits of combustibles which are sensitive to ignition energies can be substantially narrowed by reduced pressures. At elevated pressures, the lower limits of combustibles generally decrease slightly, but the upper limits tend to increase greatly. Figure 36 illustrates the effect of high pressures on the limits of natural gas (85 pct CH_4 and 15 pct C_2H_6) and ethane in air at 25° C, as reported by Kennedy (*44*). For such combustibles, the upper limits are increased at least threefold at 500 psig, above which the pressure effect diminishes; in comparison, the lower limits at 500 psig are decreased by only 1/10 or less of their values at atmospheric pressure.

Unsaturated Hydrocarbons, Aromatics, and Derivatives

The main classes of unsaturated hydrocarbons are alkenes (olefins) and alkynes (acetylenes). Flammability limits of the alkene series decrease with increasing number of carbon atoms (fig. 37), similar to the alkane series, but tend to be wider because of higher upper limits; note especially the U_{25} values in air or oxygen for ethylene (C_2H_4) versus ethane (C_2H_6) in table 6. The equivalence ratios and calorific values of their lower limits in air at 25° C are in fair agreement with those of the normal paraffins, except for ethylene, which gives noticeably lower values (table 9); values for two alkadienes, propadiene (C_3H_4) and butadiene (C_4H_6), are also included in table 9.

Many of the alkene derivatives also have wide flammability ranges, including the ethers, amines or imines, and chlorine derivatives. Data in figure 37 for three chloroethylenes show that the lower limits in air increase consistently with the number of chlorine atoms; however, their upper limits display an anomalous behavior, namely those corresponding to ethylenes with two and three chlorine atoms, i.e., dichloroethylene ($C_2H_2Cl_2$) and trichloroethylene (C_2HCl_3), respectively. Differences in heats of formation (appendix A) of these chloroethenes cannot account for this anomaly. Instead, differences in test temperatures (25° versus 100° C) and vessel diameters (5 versus 20 cm), which were more favorable for trichloroethylene, are more likely to explain these results; such variables can greatly affect the flammability of halogenated combustibles. The diameter effect is best illustrated in the flammability evaluation of trichloroethylene by Perlee (*82*). The dichloroethenes and trichloroethenes, as well as bromoethenes, have lower limit equivalence ratios and calorific ratios for combustion in air that are markedly higher than the values for their unsubstituted alkenes (table 9). Other ethene derivatives, particularly allyl alcohol (C_3H_5OH) and allyl amine ($C_3H_5NH_2$), are more consistent with the data for normal alkenes.

Alkynes present a greater flammability hazard than alkenes because of their greater thermal instability and ability to form decomposition flames with or without air. For example, acetylene vapors have a flammable range from 2.5 to 100 pct in air at 25° C and atmospheric pressure, provided the vessel diameter is at least about 15 cm (*110*); upper limits of 75 or 80 pct are occasionally given in the literature for this fuel, but these represent quenched limits from determinations in small-diameter tubes (*11*). The

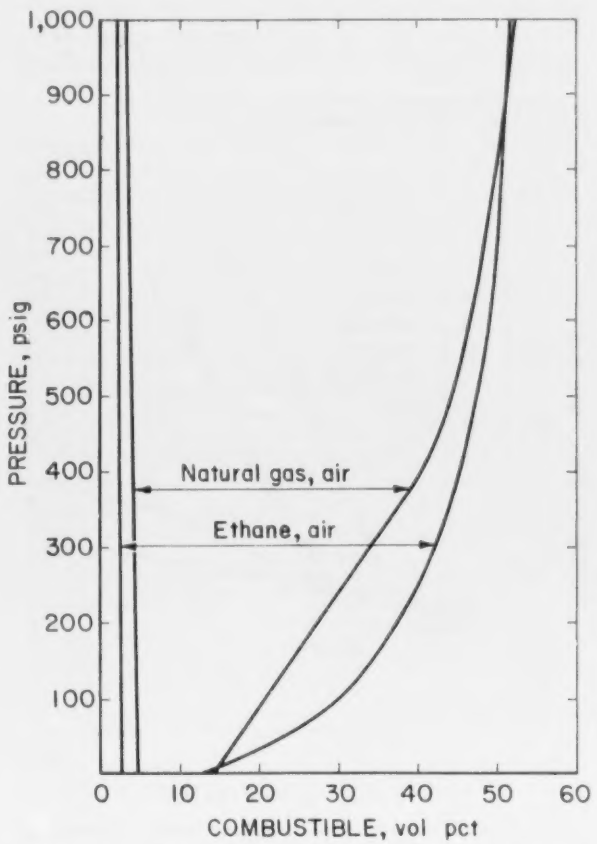


Figure 36.—Pressure effect on limits of flammability of natural gas and ethane in air at 25° C.

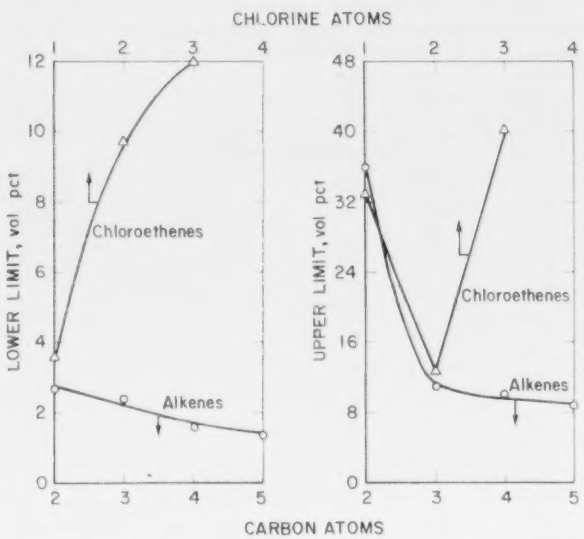


Figure 37.—Variation of lower and upper limits of flammability in air with number of carbon atoms for normal alkenes and with number of chlorine atoms for chloroethenes. Data at 25° C or reported temperature.

Table 9. — Equivalence ratios (L_{25}/C_{st}) and calorific values ($L_{25}\Delta H_c/100$) of lower limit mixtures of unsaturated and aromatic hydrocarbons and derivatives in air at 25° C and 1 atm

Formula	L_{25}, vol pct	L_{25}/C_{st}	$L_{25}\Delta H_c/100$, kcal/mol
n-ALKENES OR ALKADIENES			
C_2H_4	2.7	0.41	8.5
C_3H_6	2.4	.54	11.0
C_3H_4	2.2	.44	9.8
C_4H_8	1.6	.47	9.7
C_4H_6	2.0	.54	11.5
C_5H_{10}	1.4	.52	10.6
ALKENE DERIVATIVES			
C_2H_4O	3.6	0.47	10.5
C_2H_4NH	3.6	.60	13.0
C_2H_3Cl	3.6	.47	9.9
$C_2H_2Cl_2$	9.7	1.02	22.5
C_2HCl_3	[1]12.0	.98	25.2
C_3H_5Cl	2.9	.58	12.2
C_3H_5Br	4.4	.89	18.4
C_3H_6O	2.8	.56	12.1
C_3H_5OH	2.5	.50	10.6
$C_3H_5NH_2$	2.2	.52	10.8
$(C_2H_3)_2O$	1.7	.42	9.3
n-ALKYNES			
C_2H_2	2.5	0.32	7.5
C_2HCH_3	1.7	.34	7.5
ALKYNE (PROPARGYL) DERIVATIVES			
C_3H_3OH	2.2	0.39	9.0
C_3H_3Br	3.0	.53	11.7
ALKYL BENZENES			
C_6H_6	[2]1.3	0.48	9.8
$C_6H_5CH_3$	[2]1.2	.53	10.8
$C_6H_5C_2H_5$	[2]1.0	.51	10.5
$C_6H_5C_4H_9$	[2]82	.54	11.0
BENZENE DERIVATIVES			
$C_6H_5NH_2$	[2]1.2	0.46	9.4
$C_6H_5NO_2$	[2]1.8	.56	12.8
C_6H_5Cl	1.4	.48	10.0
$C_6H_4Cl_2$	[2]2.2	.71	14.8
C_6H_5Br	[2]1.6	.55	11.4
$(C_6H_5)_2NH$	.7	.50	10.5
$(C_6H_5)_2O$	.8	.54	11.3

[1]Limit at 30° C.
[2]Limits at elevated temperatures.

lower limit equivalence ratios for acetylene (C_2H_2) and methyl acetylene (C_2HCH_3) in table 9 are in good agreement but much lower than found for alkenes or alkanes. Halogenated alkynes such as propargyl bromide (C_3H_3Br), propargyl chloride (C_3H_3Cl), and chloroacetylene (C_2HCl) are capable of propagating flame without air at substantially lower pressures than acetylene. Even ethylene and ethylene oxide (C_2H_4O) can propagate a decomposition flame, although ethylene requires relatively high pressures (~1,000 psia). Table 10 summarizes the lower pressure limits that were reported in references 20 and 110 for various hazardous combustibles. For the hydrocarbon combustibles, their pressure limits correlate with their heats of formation (ΔH_f) and are lowest for the most endothermic (positive ΔH_f) compounds. Consistency of such correlations for any combustible will vary with the complexity of the decomposition products.

Table 10. — Lower pressure limits of flammability for combustible vapors capable of propagation without an air atmosphere[1]

Combustible	ΔH_f (25° C), kcal/mol	Vessel diameter, cm	Lower pressure limit (25° ± 5° C), cm Hg
Propargyl bromide	40	20.3	0.15
Chloroazide	NA	6.4	.2
Hydrazine	22.8	2.5	1.2
Ethyl nitrate	36.8	[2]5.3	2.5
Propargyl chloride	NA	20.3	3.0
Monochloroacetylene	51.1	5.1	6.0
Ethylene oxide	12.6	20.3	52.5
Acetylene	54.2	15.2	76
Propadiene	45.9	20.3	169
Methylacetylene	44.3	10.2	300
Ethylene	12.5	5.1	5,170

NA Not available.
[1]Selected data from references 20 and 110.
[2]Flat flame burner data.

Aromatic hydrocarbons have flammability limits that are comparable to or narrower than the values for their paraffin homologues with the same number of carbon atoms. Thus, their L_{25}/C_{st} and $L_{25}\Delta H_c/100$ values in table 9 tend to approximate the data for normal paraffins in table 7; data for dichlorobenzene ($C_6H_4Cl_2$) are the most inconsistent in these correlations.

Inorganic Combustibles

Some inorganic fuels have much wider flammability limits in ambient air than the saturated and unsaturated hydrocarbons, excluding those of high thermal instability such as the acetylenes. Such inorganics include hydrogen and carbon monoxide, which have flammability ranges of 4.0 to 75 pct and 12.5 to 74 pct, respectively, in air at 25° C and atmospheric pressure. The lower limit of 4.0 pct for hydrogen is thermodynamically impossible but is consistent with the greater diffusivity of hydrogen relative to oxygen or air. As shown by Burgess (5), preferential diffusion effects can account for the wide difference of upward and downward lower limits for hydrogen (4.0 versus 8.5 pct) and the small differences of such limits for carbon monoxide and methane. Earlier data by Furno (22) showed that similar diffusional effects can also explain the widening of upper limits of such hydrocarbons as normal butane; in this case, the greater diffusivity of oxygen allows greater fuel concentrations to be burned.

Of the nitrogen-containing inorganics, hydrazine has the widest flammability range (4.7 to 100 pct) in air and ammonia the narrowest (15 to 28 pct). As noted in table 10, hydrazine can form a decomposition flame at very low pressures, 1.2 cm Hg in a 2.5-cm-diameter tube. The flammability limits of cyanogen (6.6 to 32 pct) are nearly as wide as those for ethylene, and those for hydrogen cyanide (5.6 to 40 pct) are somewhat wider. It is worth noting that some organic nitrates and nitrites also have wide flammability limits; see appendix A and table 10. Other inorganic fuels with a wide flammability range are hydrogen sulfide (4.0 to 44 pct), carbon disulfide (1.3 to 50 pct), and diborane (0.8 to 88 pct).

The difference between the flammability limits of all combustibles tend to be less pronounced in oxygen than in air. This is evident by the available data in table 6. Similarly, the difference will be much less at highly elevated pressures, which in effect correspond to higher oxygen partial pressures.

FLAMMABILITY LIMITS IN OTHER ATMOSPHERES

The flammability limits of combustible vapors are of interest in various oxidant-inert or diluent atmospheres for defining inerting and extinguishing requirements. Complete flammability diagrams have been reported by Bureau investigators for many combustible-oxidant-inert systems. Figure 38 shows the flammability diagram given by Zabetakis (*110*) for the methane-air system with various added inerts at 25° C and atmospheric pressure. As expected, the flammability range is progressively narrowed by the addition of inert, particularly on the fuel-rich side, until propagation is not possible at some inert concentration. Helium is seen to be the least effective inert, and the halogenated hydrocarbons (CH_3Br and CCl_4) are the most effective "inerting" agents; the order of effectiveness of the other agents ($CO_2 > H_2O > N_2$) is of greater interest because of their wider use. Composites of the flammability data obtained by Coward (*11*) for five paraffin hydrocarbons are shown in figures 39 (air + N_2) and 40 (air + CO_2). These data are representative of the variations in N_2 and CO_2 inerting requirements for hydrocarbon-type combustibles, excluding such thermally unstable materials as the acetylenic hydrocarbons. Similar flammability diagrams by Jones (*40*) are given in figures 41 and 42 for hydrogen and carbon monoxide, respectively; their inerting requirements with N_2 and CO_2 are substantially greater than for most hydrocarbons.

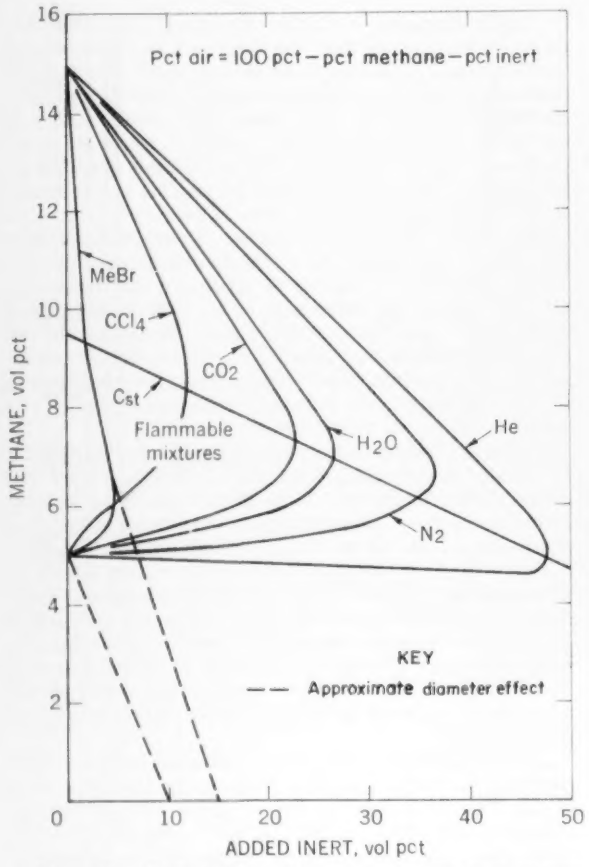


Figure 38.—Limits of flammability of various methane-air-inert gas mixtures at 25° C and 1 atm.

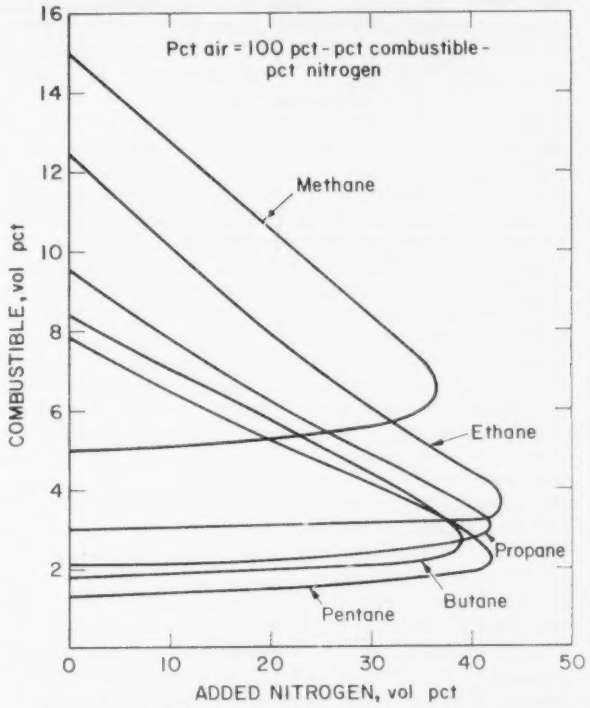


Figure 39.—Limits of flammability of methane-, ethane-, propane-, n-butane-, and n-pentane-air-nitrogen mixtures at 25° C and 1 atm.

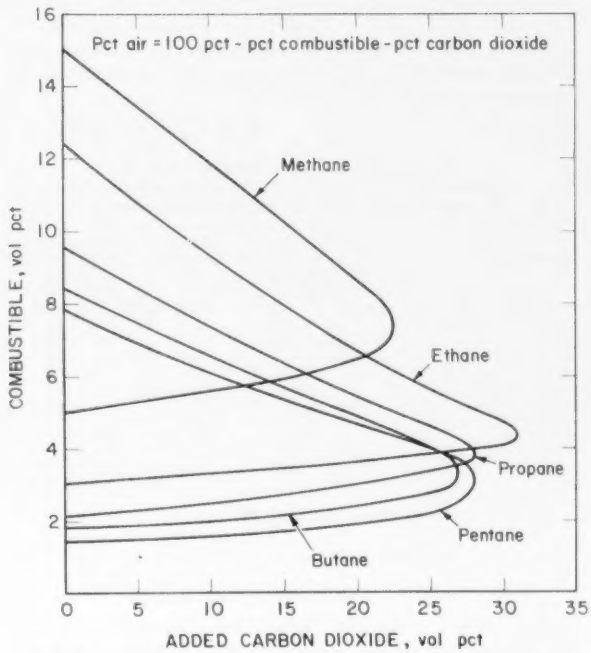


Figure 40.—Limits of flammability of methane-, ethane-, propane-, n-butane-, and n-pentane-air-carbon dioxide mixtures at 25° C and 1 atm.

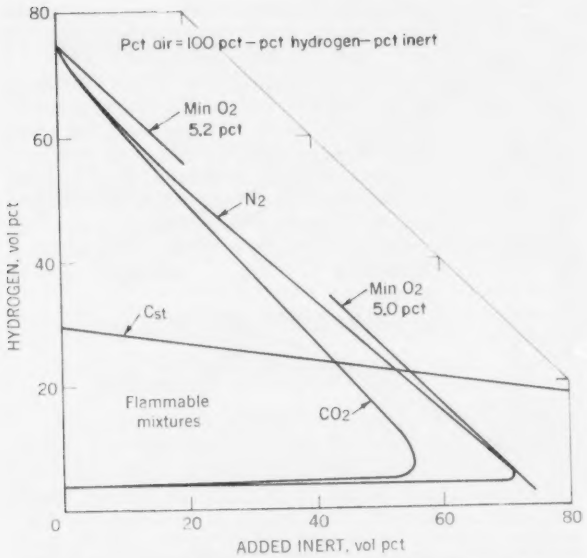


Figure 41.—Limits of flammability of hydrogen-air mixtures with added nitrogen and carbon dioxide at 25° C and 1 atm.

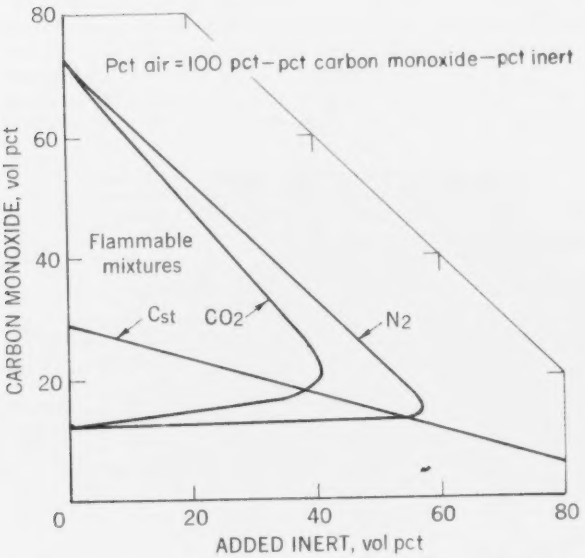


Figure 42.—Limits of flammability of carbon monoxide-air mixtures with added nitrogen and carbon dioxide at 25° C and 1 atm.

It is beyond the scope of this manual to reproduce all the complete flammability diagrams that are available for many other combustibles. Instead, such data are summarized here by listing the minimum oxygen concentrations, as defined in figure 7, below which propagation will not occur (table 11) and corresponding inert concentrations above which propagation is prevented (table 12). For the saturated hydrocarbons, their minimum O_2 values fall between 11 and 12 pct in air-N_2mixtures and between 13.5 and 14.5 pct in air-CO_2 mixtures. Practically the same range of values is found for most unsaturated hydrocarbons and hydrocarbon derivatives; those that differ significantly tend to have somewhat lower minimum O_2 values except for most of the halogenated hydrocarbons (excluding trichloroethylene). Combustibles such as hydrogen, carbon monoxide, carbon disulfide, hydrogen sulfide, and unsymmetrical dimethyl hydrazine (UDMH) stand out by their very low oxygen requirements (5 to 7.5 pct) for propagation.

Essentially the same data trends are expected in comparing the corresponding inert concentrations at the critical oxygen concentrations. The available data in table 12 for the N_2 and CO_2 inerts are consistent in this respect, except for the CO_2 value (29 pct) listed for hydrogen sulfide; this unexpected low value appears questionable. This table also includes inerting data with two Halon extinguishants, both of which are much more effective than CO_2 or N_2. Excluding ethylene, CO_2 is roughly 1-1/2 times more effective (volume basis) than N_2 in inerting the vapor-air mixtures of the saturated and unsaturated hydrocarbons. For

Table 11. — Minimum oxygen requirements for propagation of combustible vapors in air-nitrogen and air-carbon dioxide mixtures at 25° C (unless otherwise indicated) and 1 atm[1]

Combustible	Minimum oxygen concentration, vol pct	
	Air-N_2	Air-CO_2
HYDROCARBONS		
Methane	12	14.5
Ethane	11	13.5
Propane	11.5	14.5
n-Butane	12	14.5
Isobutane	12	15
n-Pentane	12	14.5
Isopentane	12	14.5
n-Hexane	12	14.5
n-Heptane	11.5	14.5
Ethylene	10	11.5
Propylene	11.5	14
α-Butylene	11.5	14
Isobutylene	12	15
Butadiene	10.5	13
3-Methyl-l-butene	11.5	14
Benzene	11	14
Cyclopropane	11.5	14
Gasoline (70/100)	12	15
Gasoline (115/145)	12	14.5
Kerosene	10 (150° C)	13 (150° C)
JP-1 fuel	10.5 (150° C)	14 (150° C)
JP-3 fuel	12	14.5
JP-4 fuel	11.5	14.5
Natural gas (Pittsburgh)	12	14.5
HALOGENATED HYDROCARBONS		
n-Butyl chloride	14	NA
Methylene chloride	17 (100° C)	NA
Ethylene chloride	13	NA
Methyl chloroform	14	NA
Trichloroethylene	9 (100° C)	NA
OTHER COMBUSTIBLES		
Acetone	11.5	14
t-Butanol	NA	16.5 (150° C)
Carbon disulfide	5	7.5
Carbon monoxide	5.5	[2]7 (5.5)
Ethanol	10.5	13
2-Ethyl butanol	9.5 (150° C)	NA
Ethyl ether	10.5	13
Hydrogen	5	[2]6 (5.2)
Hydrogen sulfide	7.5	[2]13 (11.5)
Isobutyl formate	12.5	15
Methanol	10	12
Methyl acetate	11	13.5
Methyl ether	10.5	13
Methyl formate	10	12.5
Methyl ethyl ketone	11	13.5
UDMH (dimethylhydrazine)	7	NA

NA Not available.
[1]Based upon data in references 11, 42, 54, 68, and 110.
[2]Figure in parentheses is value at upper limit in air alone.

Table 12. — Inerting requirements to prevent propagation of gaseous combustibles in air with nitrogen (N_2), carbon dioxide (CO_2), Halon 1211 (CF_2ClBr) and Halon 1301 (CF_3Br) inhibitors at 25° C (unless otherwise indicated) and 1 atm

Combustible	Minimum inerting concentration, vol pct			
	N_2[1]	CO_2[1]	Halon 1211[2]	Halon 1301[2]
HYDROCARBONS				
Methane	36	23	[3]4.0 (5.3)	[3]2.0 (4.7)
Ethane	44	31	5.8	NA
Propane	42	28	5.9	6.5
n-Butane	40	27	5.9	[4]2.9
Isobutane	40	26	5.2	8.0
n-Pentane	42	28	[4]4.5	NA
n-Hexane	41	28	5.8	NA
n-Heptane	42	28	6.5 (50° C)	8.0
Ethylene	48	39	9.6	11.0
Propylene	42	28	6.2	NA
α-Butylene	43	30	NA	NA
Isobutylene	39	26	NA	NA
Butadiene	47	34	NA	NA
Cyclopropane	41	30	NA	NA
Cyclohexane	NA	NA	5.7	NA
Benzene	44	28	4.8	4.3
Gasoline	41	28	[4]4.2	NA
Kerosene	43	28	[4]4.2	[4]2.8
JP-4	43	29	NA	6.6
OTHER COMBUSTIBLES				
Acetone	41	28	4.9	5.3
Carbon disulfide	72	59	[4]2.7	12.0
Carbon monoxide	58	41	NA	[4]1.0
Ethanol	44	31	6.2 (50° C)	4.0
Ethyl acetate	NA	NA	[4]6	4.6
Ethyl ether	48	33	NA	6.3
Hydrogen	71	57	27	20
Hydrogen sulfide	NA	29	NA	NA
Methanol	46	32	24.7 (50° C)	NA
Methyl ether	47	33	NA	NA
Methyl ethyl ketone	45	32	5.8	NA
Methyl formate	45	32	NA	NA

NA Not available.
[1]References 11, 47, and 110.
[2]References 79 and 80; includes 10-pct safety factor.
[3]Data in parentheses from reference 47.
[4]Data for flame extinguishment (less conservative value).

the same combustibles, Halon 1211 (CF_2ClBr) is about five times more effective than CO_2 and roughly comparable in effectiveness to Halon 1301 (CF_3Br). The effectiveness of the Halons is attributable to their chemical flame inhibiting action, whereas that of CO_2 and N_2 is due merely to their capacity to absorb heat. Data discrepancies are most likely to occur with the Halons because their propagations are more sensitive to vessel size and ignition energy effects. Bureau of Mines investigators (*47*) showed that the parenthetical values of 5.3 pct Halon 1211 and 4.7 pct Halon 1301 in table 12 for methane-air mixtures are more realistic than the given NFPA data (*79-80*). Figure 43 shows the complete flammability diagrams obtained by the Bureau authors with such Halons, including Halon 1202 (CF_2Br_2), in a 10-cm-diam tube (spark ignition). With a very strong and diffuse ignition source, such as an incendiary, the Halon requirements can be substantially greater. Thus, some reservation is appropriate in the use of these Halon data.

Data on the effects of temperature and pressure on inerting requirements are rather meager. The modified Burgess-Wheeler law (equation 63) may be used to obtain rough estimates of temperature effects on minimum O_2 values in air-N_2 or air-CO_2 mixtures, but its reliability for different combustibles and temperature ranges is uncertain. Ordinarily, the oxygen requirements with N_2 or CO_2 inerts decrease only slightly with moderate increases of temperature or pressure. Figure 44 (*110*) is representative

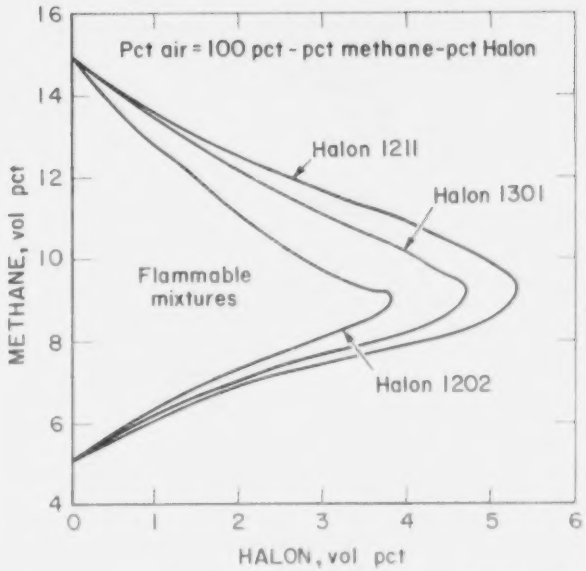


Figure 43.—Limits of flammability of methane-air-Halon mixtures at 25° C and 1 atm.

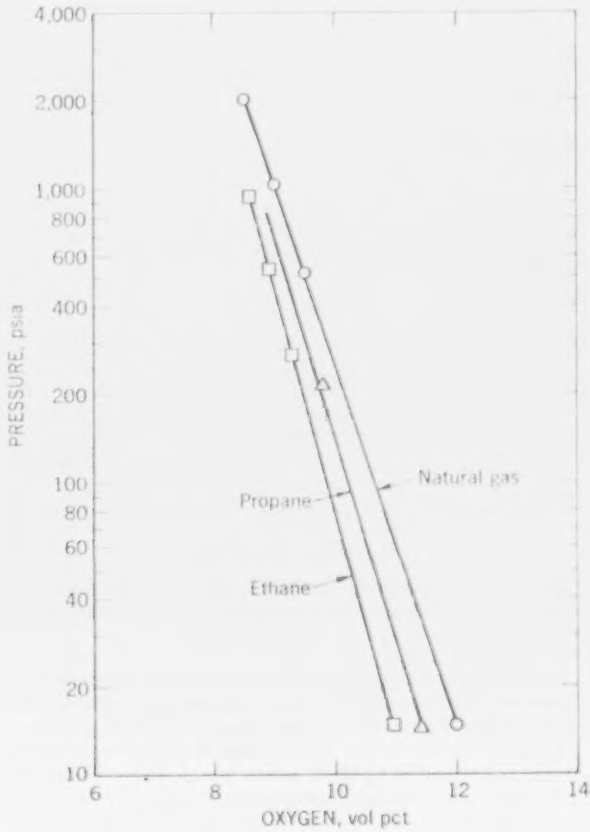


Figure 44.—Effect of pressure on minimum oxygen requirements for propagation of natural gas, ethane, and propane in air-nitrogen mixtures at 25° C.

of the pressure effect on the minimum O_2 requirements for saturated hydrocarbons in air-N_2 mixtures.

With Halon-type agents, their effectiveness may decrease greatly in propagations at even moderate pressures, depending upon their thermal stability. Both Halons and inert gases are least likely to be effective against combustibles that can propagate flame without an oxidant, such as those in table 10. Also, one must bear in mind that the inerting data are primarily applicable to the prevention of flame propagation or explosion and not for fire extinguishment, which can require much greater concentrations of extinguishants.

IGNITION REQUIREMENTS

Ignition Energies

Electrical spark ignition energies provide a measure of the thermal requirements for ignition by a highly localized source. Figure 45 presents such data from the classic studies summarized by Lewis (*66*, p. 323) for the vapor-air mixtures of six normal paraffins at 25° C and atmospheric pressure. The minimum ignition energies (MIE) for these saturated hydrocarbons are approximately 0.25 mJ and occur at fuel-air ratios greater than stoichiometric, except for methane; see also figure 4. Differences in fuel diffusivities account largely for the variation of optimum fuel-air ratios for ignition with increasing molecular weight. Lewis (*66*), Litchfield (*67-69*), and Calcote (*8*) have reported ignition energy data in air and oxygen for various combustibles, many of which are summarized in table 13. The MIE values of most combustibles fall between 0.1 and 0.3 mJ in normal ambient air. Combustibles with much lower values are acetylene, hydrogen, and carbon disulfide, and those with much higher values are ammonia and halogenated hydrocarbons, excluding butyl chloride; the MIE value for acetone is also very high but is suspect.

Corresponding MIE's in oxygen are at least an order of magnitude lower than in air. They are also very sensitive to pressure. Figure 46 shows the effects of both pressure and oxygen concentration on the MIE's of propane-oxygen-nitrogen mixtures (*66*, p. 333). The MIE's generally vary

Table 13. — Minimum spark ignition energies of combustible vapors in air and oxygen at 25° C (unless otherwise indicated) and 1 atm[1]

Combustible	Minimum ignition energy, mJ	
	Air	Oxygen
HYDROCARBONS		
Methane	0.30	0.003
Ethane	.26	.002
Propane	.26	.002
n-Butane	.26	.009
n-Hexane	.29	.006
Acetylene	.017	.0002
Ethylene	.07	.001
Propylene	.28	NA
Cyclopropane	.18	.001
Benzene	.22	NA
HALOGENATED HYDROCARBONS		
n-Butyl chloride	0.33	0.007 (88° C)
Methylene chloride	133 (88° C)	.124 (88° C)
Ethylene chloride	2.37	.011 (88° C)
Methyl chloroform	NI	.092 (88° C)
Trichloroethylene	295 (88° C)	18.0 (88° C)
OTHER COMBUSTIBLES		
Acetaldehyde	0.38	NA
Acetone	1.15	0.0024
Ammonia	>1,000	NA
Carbon disulfide	.015	NA
Ethyl ether	.20	.0013
Ethylene oxide	.062	NA
Hydrogen	.017	.0012
Hydrogen sulfide	.077	NA
Methanol	.14	NA
Propylene oxide	.14	NA

NA Not available. NI No ignition.
[1] Based upon data in references 8, 66 (p. 323), and 67-69; mixture composition stoichiometric or near-optimum for ignition.

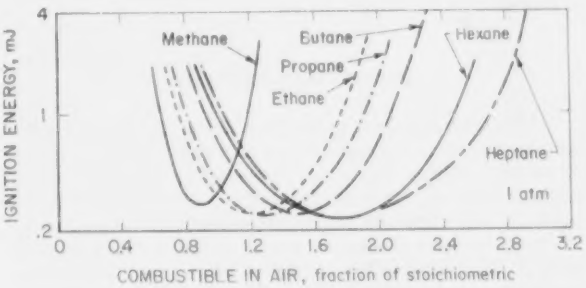


Figure 45.—Spark ignition energy versus combustible vapor concentration for six paraffins in air at atmospheric pressure.

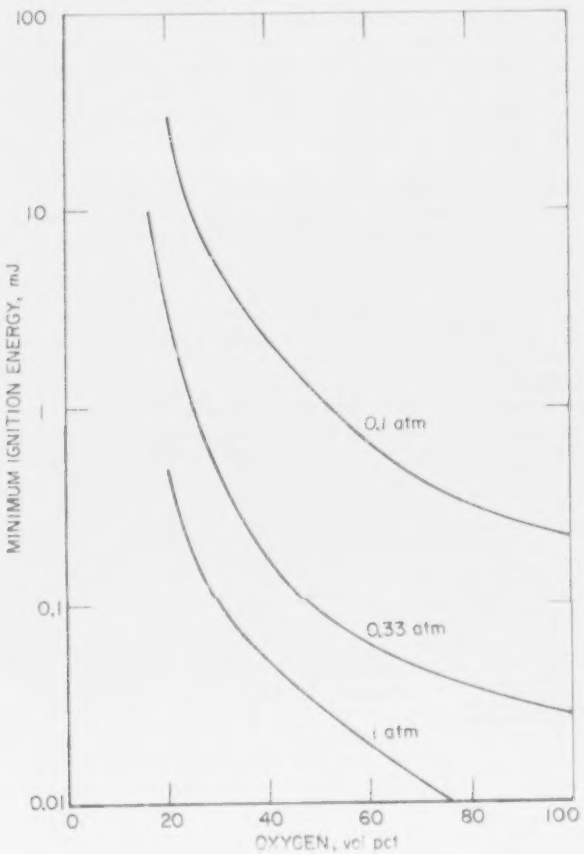


Figure 46.—Minimum spark ignition energy of propane-oxygen-nitrogen mixtures as a function of oxygen concentration and mixture pressure.

inversely with approximately the square of pressure. With increasing temperature, they decrease roughly by a factor of 2 for a 100° C temperature change (*69*). The low ignition energy requirements of combustible vapor mixtures are of great concern since sparks or arcs from ordinary electrical equipment have much greater energies (order of joules); even spark energies from static electricity are often greater (order of tens of millijoules) than MIE values, as discussed under theory and definition. Applications of spark ignition data to safety engineering, including intrinsic safety, are elaborated on by Litchfield (*67*).

Quenching Distances

Minimum ignition quenching distances for the combustible vapors in normal ambient air or oxygen are included in table 14. These data were obtained by the above-cited authors and refer to quenching of the spark flame kernel between flat plate electrodes. As with MIE values, minimum quenching distances occur at near-stoichiometric fuel-air ratios and fall in a narrow range (~1.5 to 2.5 mm) for many combustibles. Notable exceptions again are acetylene, carbon disulfide, and hydrogen, which are the most readily ignitable; other exceptions are ammonia and some of the halogenated materials, which are least ignitable.

Although corresponding data in oxygen are less available, the minimum quenching distances are much lower, being only a few tenths of a millimeter for hydrocarbons and hydrogen (table 14). For most combustibles, quenching distances vary inversely with the first power of pressure but with an ill-defined power of temperature (*69*). A useful correlation for estimating the minimum ignition quenching distance from the MIE, or vice versa, is given graphically by figure 47 (*102*). This figure is a composite of Bureau data for various combustible-oxidant-diluent mixtures over a wide range of pressures and oxygen concentrations; here, the MIE varies approximately with the square of the quenching distance. Quenching diameters obtained in tubes are about 1.5 times greater than these flat plate quenching distances.

Such ignition quenching data are useful in predicting flame propagation hazards of combustible mixtures and designing flame arresting devices. An effective flame arrester must quench the propagating flame at the arrester face and remove sufficient heat from the product gases to prevent ignition beyond the arrester; thus, both flame velocity and arrester physical specifications are important. In practice, flame velocities can be much greater than those developed in the above quenching distance experiments. Palmer (*81*) found the approach velocity of the flame to be most critical and developed semiempirical expressions for predicting the effectiveness of various flame arresters.

Table 14. — Comparison of minimum spark ignition quenching distances and maximum experimental safe gaps (MESG) of combustible vapors in air at 25° C and 1 atm[1]

Combustible	Ignition quenching[2] distance, mm	MESG[3], mm
HYDROCARBONS		
Methane	2.03 (0.30 in O_2)	1.14
Ethane	1.5	.91
Propane	1.75	.92
n-Butane	2.4 (0.15 in O_2)	.98
n-Hexane	1.5 (0.20 in O_2)	.93
Acetylene	.64 (0.18 in O_2)	.37
Ethylene	1.22 (0.23 in O_2)	.65
1,3-Butadiene	1.25	.79
Cyclopropane	NA	.91
Benzene	1.95	.99
HALOGENATED HYDROCARBONS		
Allyl chloride	<2.75	1.17
n-Butyl chloride	2.2	1.06
Methylene chloride	5.46	NA
Ethylene chlorirte	4.57	1.8
Vinyl chloride	NA	.96
OTHER COMBUSTIBLES		
Ammonia	NI	3.18
Carbon disulfide	.55	.20
Carbon monoxide	NA	.91
Ethyl ether	1.85	.83
Isopropyl ether	3.0	.94
Ethylene oxide	1.18	.59
Hydrogen	.64 (0.25 in O_2)	.20
Methanol	1.5	.92
Methyl amine	NA	1.10
Propylene oxide	1.3	.70
Vinyl acetate	2.35	.94

NA Not available. NI No ignition at 1 J.
[1]Mixture composition—stoichiometric or near-optimum for ignition.
[2]Reference 8, 66 (p. 323), and 67-69.
[3]Reference 71.

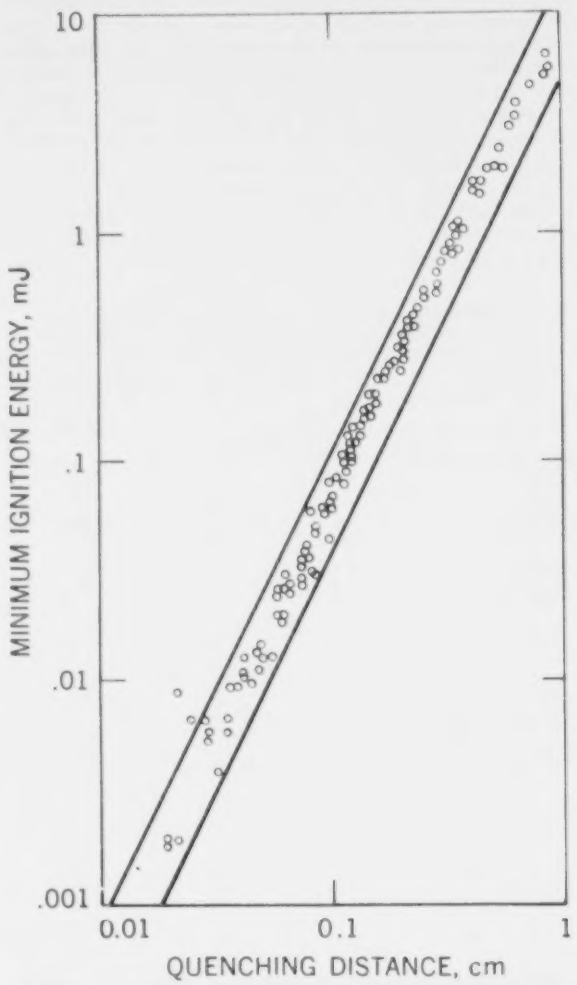


Figure 47.—Correlation of minimum ignition energy with minimum quenching distance for a large variety of combustibles in air and other oxidant atmospheres.

Based on this work and others, a simple relationship is given in a British guide (*73*) for predicting the critical approach velocity:

$$v = 0.5\ a\ y/d^2, \qquad (65)$$

where v is flame velocity (ft/s), y is arrester thickness (in), d is diameter of apertures (in), and a is the face area not blocked by the arrester material (wire gauze, metal ribbon, etc.). This expression is primarily applicable to ordinary flame propagations and to moderate pressures.

In the case of explosionproof enclosures, ignition quenching distance data are not sufficiently conservative to protect against the high-velocity jets of flame or hot gas that can be produced at high explosion pressures. Instead, it is necessary to use the maximum experimental safe gap (MSEG) data, which are designed to prevent ignition by any jets of hot gas escaping through the flange gap of such enclosures; hot gas ignition temperatures are given in the next section. The MSEG values included in table 14 are proposed by British Government laboratories (*71*) and were obtained at an initial pressure of 1 atm and gap passage length of 2.54 cm (1 in). Underwriters' Laboratories (*15*) in this country reports lower MSEG values for some of the combustibles, particularly acetylene, hydrogen, carbon disulfide, and ammonia. Their lower values reflect the effects of a shorter gap length (3/4 in) and more severe explosion pressures that were developed by using turbulent mixtures and a long flame runup to simulate pressure piling.

Ignition Temperatures

Minimum autoignition temperatures (AIT's) are widely relied upon for assessing the ignitability hazard of combustible vapors in a heated environment without an external ignition source. Relatively complete listings of AIT's for liquid and gaseous compounds in atmospheric air are given in appendix A. These listings also update any previously reported data that could not be confirmed, including the widely cited values for methane (540° C) and hydrogen (400° C). The data refer to ignitions under static conditions that were obtained in open glass vessels, usually of at least 200 cm^3 volume and with induction or contact times (ignition delays) of the order of minutes; data obtained in smaller vessels or with shorter contact times are less conservative for safety applications. Appearance of any flame was normally used as the criterion of ignition in such determinations. Precision of these data can be assumed to be approximately ± 10° at 300° C. They should not be confused with flashpoints, which relate to the volatility and not the ignitability of the combustible.

AIT's of combustibles are lower in oxygen than in air, but the differences are not great for most hydrocarbon combustibles. Selected data from Bureau (*23, 110, 112*) and NFPA (*72, 78*) compilations are given in table 15 for some representative organic and inorganic combustibles at atmospheric pressure. The effects of chemical structure are evident from the data in this table and appendix A. Generally, the AIT's of straight-chain hydrocarbons decrease with increasing number of carbon atoms and increase with chain branching (note isobutane) and ring formation (note cyclopropane); Zabetakis (*112*) showed they can be correlated with the average chain length. Similar trends occur with the various families of hydrocarbon derivatives, although the data are less consistent, depending upon the functional group. The AIT's of most hydrocarbons and their derivatives in air fall between the values for methane (630° C) and n-decane (210° C); notable exceptions are acetaldehyde, methyl hydrazine, and various alkyl ethers, nitrites, or nitrates, which can autoignite below 200° C. Among inorganic compounds, the AIT's are lowest for carbon disulfide and diborane (≤100° C) and highest for carbon monoxide and ammonia (>600° C); the updated values for hydrogen are 520° C in air and 400° C in oxygen. With nitrogen tetroxide as the oxidant, the AIT's are comparable to those in oxygen for such paraffins as butane, hexane, and heptane, but lower by 100° to 200° C for hydrogen and highly chlorinated hydrocarbons (*23*); also, hydrazine fuels are hypergolic with this oxidant.

Table 15. — Minimum autoignition temperatures (AIT's of combustible gases and liquids in air and oxygen at 1 atm

Combustible	Minimum AIT, °C	
	Air[1]	Oxygen[2]
HYDROCARBONS		
Methane	630	555
Ethane	515	505
Propane	450	NA
n-Butane	370	285
Isobutane	460	320
n-Pentane	260	260
n-Hexane	225	220
n-Heptane	225	210
n-Octane	220	210
n-Decane	210	200
Acetylene	305	295
Ethylene	490	485
Propylene	460	425
1,3-Butadiene	420	335
Cyclopropane	500	455
Gasoline (100/130)	440	315
Kerosene	230	215
HALOGENATED HYDROCARBONS		
Ethyl chloride	520	470
n-Butyl chloride	250	245
Methylene chloride	615	535
Ethylene chloride	440	430
Methyl chloroform	485	470
Trichloroethylene	420	405
OTHER COMBUSTIBLES		
Acetaldehyde	175	160
n-Amyl acetate	360	235
Carbon disulfide	100	105
Carbon monoxide	610	590
Ethyl ether	195	180
Glycerol	370	320
Hydrazine	270	150
Hydrogen	520	400
Hydrogen sulfide	260	220
Propanol	440	330
Vinyl ether	360	165

NA Not available.
[1]References 72, 110, and 112.
[2]References 23 and 78.

Figure 48 (*57*) illustrates the dependence of ignition delays on autoignition temperatures in stagnant air for various hydrocarbon fuels, including cyclics and aromatics. Although the data display an exponential dependence as predicted by the Semenov theory (equation 29), the temperature dependence for each fuel changes to a less sensitive one (decreased slope) at some high temperature; this indicates a change in reaction mechanisms or rate-controlling factors. Global activation energies (E) derived from the slopes and use of equation 29 are 11 to 22 kcal/mol in the high-temperature region and 33 to 46 kcal/mol in the low-temperature region for most of these fuels. Similar data under flow conditions, where contact times can be of the order of milliseconds, are rather meager for individual compounds. The following expressions from the above Bureau work (*57*) give the approximate variation of ignition delay

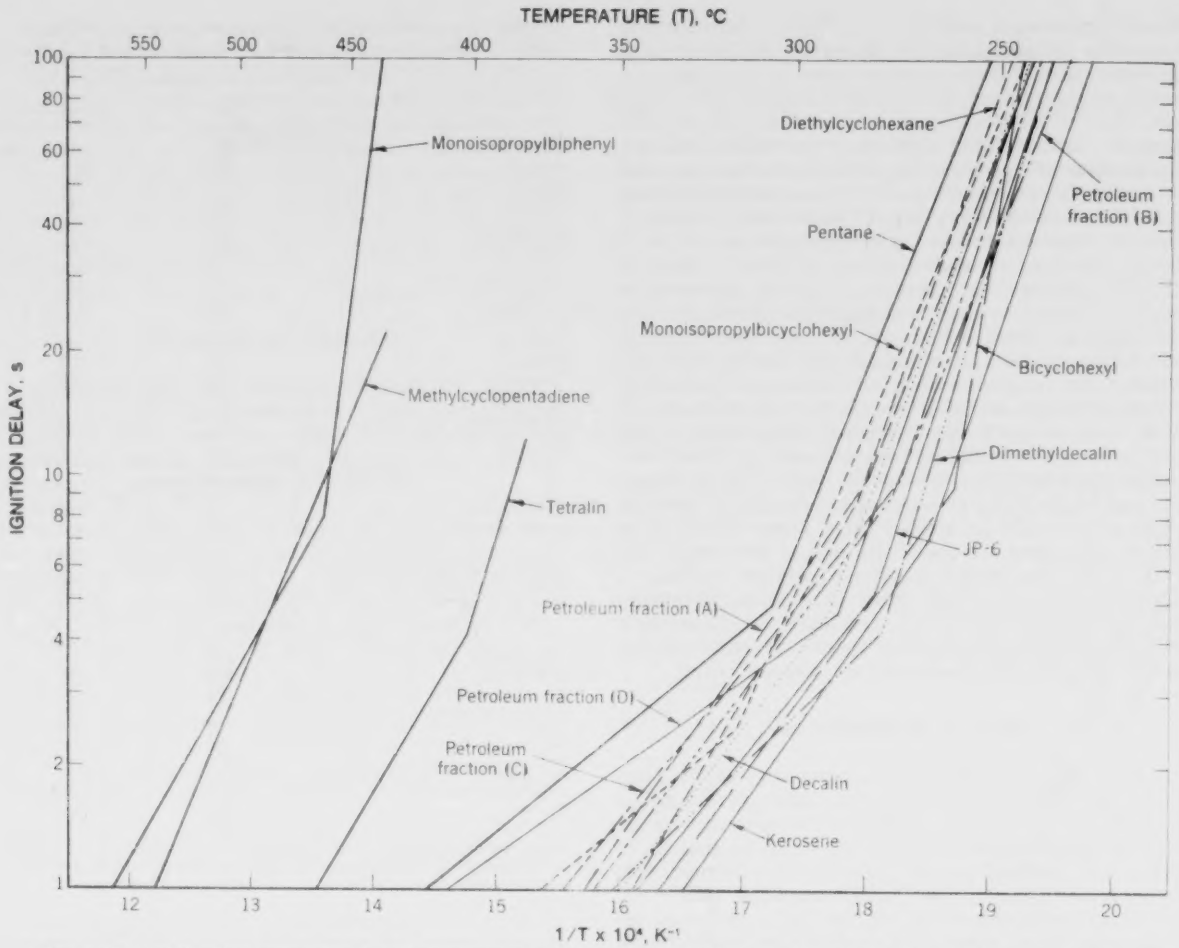


Figure 48.—Autoignition temperatures and corresponding ignition delays of hydrocarbon fuels under static conditions in air at atmospheric pressure.

(τ, ms) with temperature (T, K) for n-pentane (C_5H_{12}) and decalin ($C_{10}H_{18}$) in heated air streams at 2 atm:

$$\text{Pentane (350°-650° C)} \;..\; \ln \tau = 5400/RT + 1.13 \quad (66)$$

$$\text{Decalin (370°-600° C)} \;..\; \ln \tau = 6600/RT - 0.37 \quad (67)$$

where R is 2 cal/(K·mol). The low gross activation energies indicate that physical factors rather than chemical factors were rate controlling.

Autoignition temperatures decrease with increasing pressure, but the decrease is often small for moderate pressure changes, depending upon the combustible and oxidant. According to data for high-molecular-weight hydrocarbons (*57*), their AIT's in air at 5 atm roughly approximate their corresponding values in oxygen at atmospheric pressure (table 15), i.e., an atmosphere of equivalent oxygen partial pressure. Also, the values in air for hydrocarbons of low AIT (~250° C) are approximately doubled when the pressure is reduced to 0.5 atm (*57, 112*). However, as shown by Furno (*23*) for selected paraffins, chlorinated hydrocarbons, and hydrazine fuels, the pressure effect is greatly diminished by the use of large vessels (4,900 cm^3).

Ignitions by any heated surface are a function of the heat source dimensions. For autoignitions in heated vessels, a vessel diameter of at least 5 cm or surface-volume ratio (S/V) less than 1 cm^{-1} is required to obtain the AIT values given in appendix A. With larger vessels, Setchkin (*94*) has shown that the AIT's do not decrease greatly, although the size effect can still be significant for some combustibles. Heated wire, rod, or tube ignition temperatures are normally much higher than the heated vessel AIT's; such data are compared in table 16 for some representative combustibles. Figure 49 was obtained by Kuchta (*50*) and illustrates the dependence of ignition temperature on surface area of the heat source with different sources and combustibles; heat source diameters ranged from 0.8 to 7.5 cm for the vessels (cylindrical) and from 0.04 to 2.5 cm for the wires or rods. For the three paraffins in this figure, their ignition temperatures (T, °C) in air are given by the following expressions for heat source surface areas (A, cm^2) less than 80 cm^2:

n-Hexane	$T = 951 - 98.5 \ln A;$	(68)
n-Octane	$T = 921 - 96.0 \ln A;$	(69)
n-Decane	$T = 893 - 89.5 \ln A.$	(70)

Table 16. — Comparison of hot surface and hot gas ignition temperatures of hydrogen, carbon monoxide, and hydrocarbon fuels in air at 1 atm

Combustible	Ignition temperature, °C			
	Heated[1] glass vessel (~4.5-cm diam)	Heated[2] Inconel wire (1-cm diam)	Heated[3] Nichrome wire (0.1-cm diam)	Heated[4] air jet (1-cm diam)
Methane	630	NA	1,220	1,040
Ethane	515	NA	980	840
Propane	450	NA	1,050	885
n-Butane	370	NA	1,010	910
n-Hexane	225	670	900	765
n-Octane	220	660	860	755
n-Decane	210	650	835	750
Acetylene	305	NA	850	655
Ethylene	490	NA	900	765
Propylene	460	NA	1,090	930
Isobutylene	445	NA	1,060	960
Carbon monoxide	610	NA	780	785
Hydrogen	520	NA	750	640
JP-6 fuel	230	695	930	805
MIL-L-7808 oil	390	585	695	750

NA Not available.
[1]AIT data from table 15 and appendix A.
[2]Reference 50.
[3]References 50 and 103.
[4]References 51 and 103.

Linear correlations extending to the larger surface areas (~180 cm^2) associated with heated vessel AIT's appear to occur only with combustibles requiring high autoignition temperatures; note data for the engine oil.

Heat source dimensions are equally important in ignitions by jets of hot gases that may come into contact with a combustible vapor-air mixture. Comprehensive studies on hot gas ignitions have been made by Vanpee and Wolfhard (*103-104, 108*). Their results on the effect of jet diameter on ignition temperature with heated laminar air jets are shown in figure 50 for hydrogen and the lower members of the alkane and alkene series; similar data for higher alkane members are also available (*51*). Minimum ignition temperatures obtained with a 1-cm-diam heated air jet are included in table 16 for the various combustibles. As noted, the hot gas ignition temperatures correlate best with the heated wire or rod ignition temperatures, all of which are noticeably higher than the heated vessel AIT's. In comparing all such ignition temperatures for a given combustible, Kuchta (*51*) found the differences are not necessarily great when they are compared at the same heat source diameter. Hot gas ignition temperatures are especially useful in evaluating the ignition hazard of possible hot gases evolved from flame arrestors, explosionproof seals, and permissible explosive firings in mines.

FLAME TEMPERATURES AND BURNING RATES

Flame Temperatures

Assessment of the potential heat release and pressure development in the combustion of gaseous mixtures requires a knowledge of flame temperatures. Table 17 includes such data for the constant-pressure combustion of various combustibles in ambient air at atmospheric pressure; the

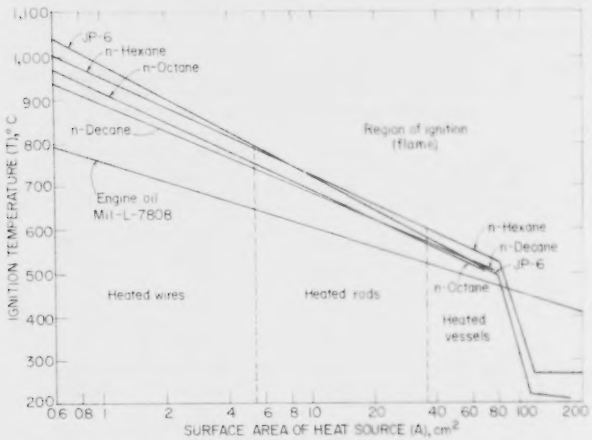


Figure 49.—Hot surface ignition temperatures as a function of heat source surface area for hydrocarbon fuels and an engine oil in air at 1 atm.

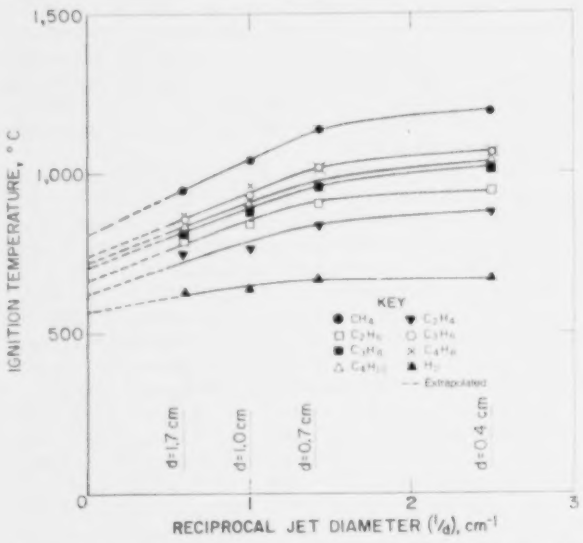


Figure 50.—Hot gas (air) ignition temperatures as a function of reciprocal jet diameter for hydrogen and various hydrocarbons at atmospheric pressure.

Table 17. — Limit flame temperatures, maximum flame temperatures, and maximum burning velocities of gaseous combustibles in air at 1 atm

Combustibles	Limit flame temperature, $(T_f)_L$		Maximum flame[1] temperature, $(T_f)_M$		Maximum burning[2] velocity (S_u), cm/s
	Diffusion[3], °C	Premixed[4], °C	Measured, °C	Calculated, °C	
HYDROCARBONS					
Methane	1,518	1,377 (1,260)	1,875	1,927	45
Ethane	1,363	1,327 (1,230)	1,895	1,922	47.5
Propane	1,422	1,367 (1,310)	1,925	1,967	45.5
n-Butane	1,434	1,492 (1,390)	1,895	2,007	46
n-Pentane	NA	1,362	NA	2,002	44.5
n-Heptane	NA	~1,400 (1,370)	NA	2,002	42.5
Acetylene	NA	1,002	2,325	2,307	157
Ethylene	1,335	1,202	1,975	2,067	74.5
Propylene	1,489	1,337	1,935	2,047	51
Butylene	1,494	NA	1,930		43
1,3-Butadiene	NA	1,317	NA	2,104	54.5
Cyclopropane	NA	1,377	NA	2,077	55.5
Cyclohexane	NA	NA	NA	1,952	43.5
Benzene	1,540	1,442	NA	2,092	48
Natural gas	NA	~1,350	NA	1,950	38.5
OTHER COMBUSTIBLES					
Acetone	NA	1,427	NA	1,934	42.5
Acrolein	NA	1,267	NA	2,067	66
Carbon monoxide	1,177	NA	2,100	2,032	52
Ethanol	1,405	NA	NA	NA	NA
Ethyl ether	1,386	1,337	NA	2,032	50
Ethylene oxide	NA	1,242	NA	2,152	89.5
Hydrogen	811	712	2,045	2,072	326
Methanol	1,258	NA	NA	1,862	57
Propylene oxide	NA	1,282	NA	2,087	67

NA Not available.
[1]References 66, p. 705 (measured values) and 2, 18, and 95 (calculated values); values for near-stoichiometric mixtures.
[2]References 2, 25, and 95; values for near-stoichiometric mixture.
[3]Reference 103 (diffusional burner flame method).
[4]Reference 18 (flammability tube method); parenthetical values from reference 115.

maximum flame temperatures were obtained with near-stoichiometric mixtures. Measured values by Lewis (*66*, p. 628) differed only slightly (<100° C) from calculated values for common hydrocarbons in spite of the lack of adiabatic conditions in measuring such temperatures. Calculated data by Fenn (*18*), Simon (*95*), and others (*2*) are included in table 17. Excluding acetylene (2,325° C), the maximum flame temperatures of hydrocarbons and their derivatives fall in a narrow range, nominally between 1,900° and 2,100° C; hydrogen and carbon monoxide also fall within this temperature range. Corresponding flame temperatures under constant-volume conditions are about 20 pct higher, largely because of the heat capacity differences of the gaseous products under constant volume and constant pressure; see equations 40 and 42.

Limit flame temperatures for the constant-pressure propagation of combustible vapor-air mixtures (lower limit mixtures) are also included in table 17. It is evident that the premixed flame data by Fenn (*18*) and Zabetakis (*115*) are more conservative than the diffusional flame data by Vanpee (*103*). A temperature of at least 1,200° C is required by most of these combustibles, excluding acetylene (~1,000° C) and hydrogen (~800° C). Lowest flame temperatures occur at the lower flammability limit that correspond to upward propagation and constant-pressure combustion. However, in the special case of hydrogen, which has a very high diffusivity coefficient, the calculated flame temperature for its lower limit in air with upward propagation (4.0 pct) would be less than 400° C. Thus, a value of 700° to 800° C is more meaningful and would be characteristic of the concentration required for downward propagation (~8 pct). The variation of theoretical flame temperatures and pressure rises for the adiabatic combustion of hydrogen, methane, and carbon monoxide in atmospheric air is shown in table 18 as a function of combustible concentration. Furno (*22*) and Burgess (*5*) showed that the experimental and theoretical explosion pressures come into agreement only when upward and downward propagation can occur. Knowing the flame temperature at constant volume, the explosion pressure can be estimated by use of equation 48. Thus, for a 5 pct methane-air mixture, the calculated explosion pressure is

$$P_2 = P_1 \frac{n_2}{n_1} \frac{T_2}{T_1} = 1 \times 1 \times \frac{1{,}810}{300} = 6.03\ \text{atm}, \qquad (71)$$

where P is in atm, T is in K, and n_2/n_1 is 1. A maximum P_2/P_1 ratio of approximately 8 is typical of near-stoichiometric mixtures.

Table 18. — Calculated flame temperatures and pressure rises for adiabatic combustion of hydrogen, methane, and carbon monoxide in air at 25° C (*5*)

Fuel concentration, vol pct	Pressure rise (ΔP), psig	Flame temperature (T_f), K	
		Constant volume	Constant pressure
H_2-air:			
4	21.4	746	628
6	30.9	951	788
8	39.8	1,151	944
12	56.2	1,528	1,249
15	67.2	1,794	1,472
CH_4-air:			
4.5	68.5	1,688	1,382
5	74.6	1,810	1,485
6	86.0	2,040	1,683
7	96.4	2,248	1,870
8	105.4	2,425	2,043
CO-air:			
10	53.2	1,450	1,194
11	57.4	1,547	1,275
12	61.5	1,643	1,355
13	65.4	1,736	1,434
14	69.2	1,828	1,512

Burning Velocities

Like flame temperatures, burning velocity (S_u) of a flammable mixture is a fundamental property and depends primarily upon the temperature, pressure, and composition of the mixture. The burning velocities of limit vapor-air mixtures are only a few centimeters per second and become maximum at near-stoichiometric combustible concentrations. Figure 51 illustrates the combustible concentration effect obtained by Gibbs (*25*) for several paraffins in air at ambient temperature and pressure. Maximum S_u values are given for these and other combustibles in table 17. The maximum values for the paraffins and most of their derivatives fall in the 40- to 50-cm/s range, whereas those for unsaturated hydrocarbons are usually greater. Values for acetylene (155 cm/s), hydrogen (325 cm/s), ethylene (75 cm/s), and ethylene oxide (90 cm/s) stand out among the fast-burning combustibles.

With the addition of inert diluents, burning velocities decrease depending upon the concentration and heat capacity of the diluent. Figure 52 (*92*) shows the effect of added nitrogen on both burning velocity (S_u) and flame speed (S_f) of methane-air-N_2 mixtures. Greater S_u reduction occurs with inerts of greater heat capacity than N_2 and even more so with diluents that are chemical flame inhibitors; Johnson (*39*) found that 2.4 pct Halon 1301 (CF_3Br) gave approximately the same S_u reduction (~85 pct) as 34 pct N_2 for CH_4-air flames at near-atmospheric pressure. Assuming nonturbulent flames, the maximum flame speeds of most combustibles at optimum fuel-air ratios can be roughly estimated by

$$S_f = 8\,S_u, \qquad (72)$$

where 8 approximates the expansion ratio (see equation 45) for combustion at 25° C and atmospheric pressure.

Burning velocities are much higher in oxygen than in air. For the paraffins, the maximum values at normal ambient conditions are about an order of magnitude greater in oxygen, as shown in figure 53 from the work by Singer (*96*). For such fuels as acetylene, hydrogen, and carbon monoxide, the corresponding values are about 7, 4, and 2-1/2 times greater, respectively, in oxygen than in air.

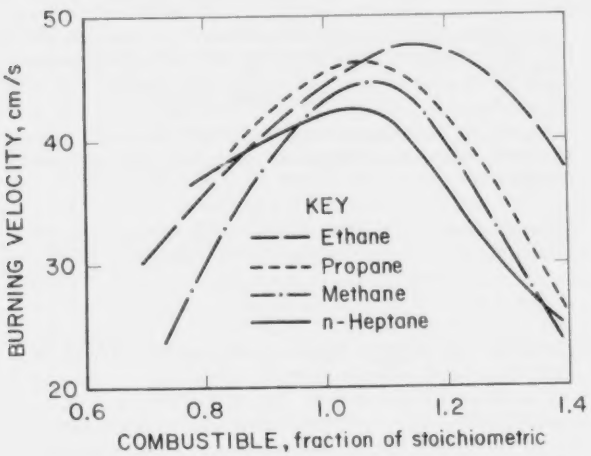


Figure 51.—Burning velocities of methane-, ethane-, propane-, and n-heptane-air mixtures at atmospheric pressure and room temperature.

These data are summarized in the comprehensive works by Lewis (*66*, p. 705) and Gaydon (*24*, p. 56), who have developed basic theories on flame propagation. With increasing temperature, the burning velocities increase (fig.

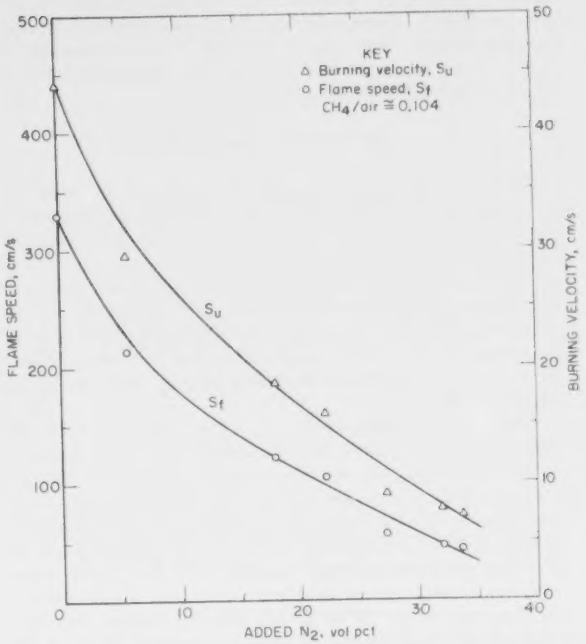


Figure 52.—Burning velocity and vertical flame speed versus added N_2 for combustion of CH_4-air-N_2 mixtures in a 3.65-m (12-ft) diam sphere at 25° C and 1 atm.

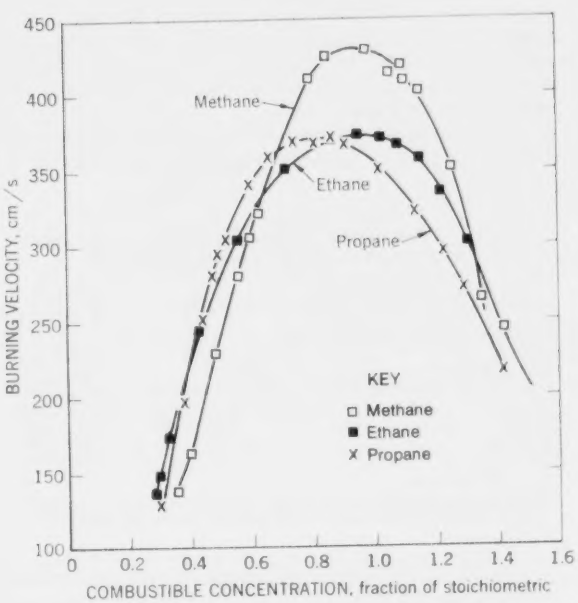


Figure 53.—Burning velocities of methane-, ethane-, and propane-oxygen mixtures at atmospheric pressure and room temperature.

54). The following expression by Dugger (*16*) has been found reliable for at least paraffinic hydrocarbons in ambient air:

$$S_u = 10 + 0.000342\ T^2 \qquad (73)$$

where S_u is in cm/s and T is in K. Pressure effects on S_u are more difficult to predict. Data summaries (*24, 66, 110*) indicate that S_u decreases with increased pressure for low-burning-velocity mixtures (<50 cm/s) and increases for high-velocity mixtures (>100 cm/s); intermediate mixtures display little effect of pressure.

Detonation Velocities

Detonations involve supersonic propagation rates and are more likely to occur in oxygen than in air. Figure 55 gives the detonation velocities obtained by Morrison (*74*) for vapors of various paraffins in oxygen as a function of combustible concentration. Maximum velocities are 2,500 to 2,700 m/s for these combustibles. For acetylene, hydrogen, and ammonia, the maximum values are closer to 3,000 m/s or more (*66*, p. 524). In all cases, the maximum values occur at combustible concentrations greater than stoichiometric.

Many combustibles can also undergo detonation in air, although this requires much higher initiation energies, higher pressures, or conditions that promote turbulent combustion and pressure piling. Propagations in long tunnels, especially with irregular wall surfaces, offer favorable conditions for detonations. Although detonations of the paraffins are obtained most readily with the higher members, even methane-air mixtures have been found detonable in recent work. Table 19 lists the detonation velocities obtained by Burgess (*6*) in an air atmosphere for a few hydrocarbon fuels; data for methane and hydrogen are taken from references 46 and 66, p. 524. Although the velocities in air are lower than in oxygen, they are all above 1,500 m/s over the given range of concentrations, below or above which they decrease as the detonability limits are approached; detonability limits normally fall within flammability limits but can be wider for some combustibles with the use of large booster (initiator) charges. In addition to the initiator strength, the length and diameter (or l/d ratio) of the explosion container can be critical for the development of a detonation at a given pressure; detailed discussions of these factors are given in references 66 and 110.

Table 19. — Detonation velocities of several combustibles in air at 25° C and atmosphere pressure[1]

Combustible	Combustible concentration, vol pct	Initiator	Detonation velocity, m/s
Acetylene	19-77	10 g PETN	1,950-2,100
Ethylene oxide	10-18	10 g tetryl	1,890-1,910
	20.5-22	100 g tetryl	2,300-2,350
Hydrogen	~30	NA	1,975
Methane	7-13	50-70 g Amatol	1,550-1,600
Propane	4-7	10 g PETN	1,800-1,890
MAPP gas[2]	6-8	10 g PETN	1,800-1,850

NA Not available.
[1]Based upon data in references 6, 46, and 66, p. 524.
[2]Methylacetylene, propadiene, and propane of near-equal fractions.

Additional detonation velocities for various combustible mixtures are listed in table 20. Although these data were compiled by Laffitte (*61*) almost 50 years ago, they are in fair to good agreement with more recent data, including those given in figure 55 for the paraffins. Where data

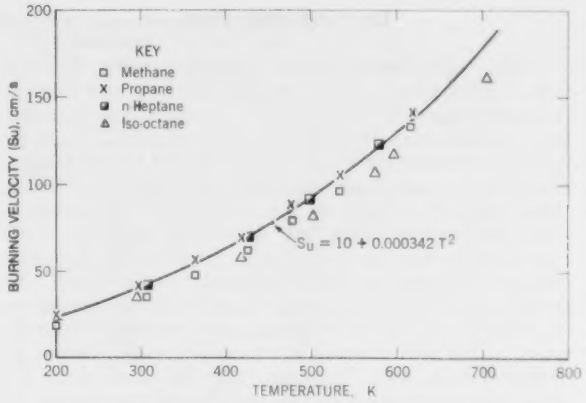


Figure 54.—Effect of temperature on burning velocities of four paraffins in air at atmospheric pressure.

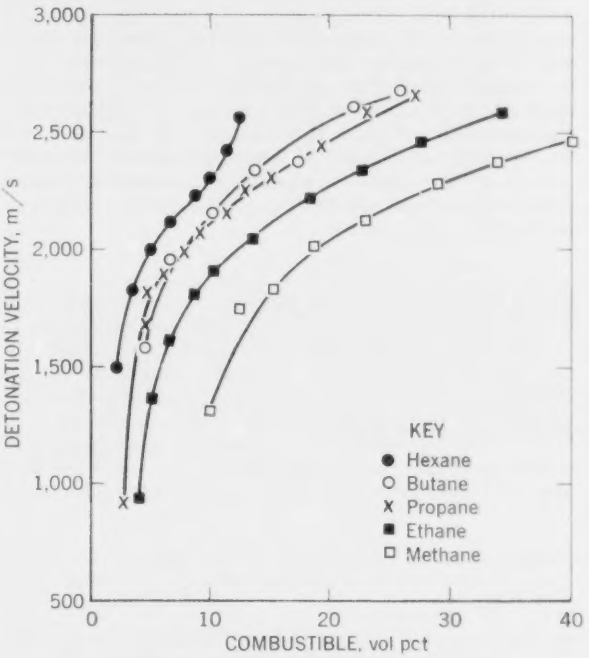


Figure 55.—Detonation velocities of methane-, ethane-, propane-, butane-, and hexane-oxygen mixtures at atmospheric pressure.

discrepancies occur, the values in table 20 are on the low side. It is worth noting that the detonation velocities of benzene and ethyl alcohol at stoichiometric oxygen concentrations are comparable to those of most hydrocarbons, excluding acetylene. Other combustibles such as carbon monoxide and carbon disulfide have relatively low detonation velocities in oxygen even at stoichiometric concentrations; the value for carbon monoxide (1264 m/s) is near marginal for a true detonation. Because of the magnitude of detonation velocities, explosion protection systems designed to protect against deflagrations (subsonic) can hardly be expected to be effective against detonations (supersonic).

Table 20. — Detonation velocities of various combustible mixtures at 25° C and atmospheric pressure (*61*)

Mixture	Detonation velocity, m/s	Mixture	Detonation velocity, m/s
$2H_2 + O_2$	2,821	$C_3H_8 + 3\ O_2$	2,600
$2\ CO + O_2$	1,264	$C_3H_8 + 6\ O_2$	2,280
$CS_2 + 3\ O_2$	1,800	$i\text{-}C_4H_{10} + 4\ O_2$	2,613
$CH_4 + 2\ O_2$	2,146	$i\text{-}C_4H_{10} + 8\ O_2$	2,270
$CH_4 + 1.5\ O_2 + 2.5\ N_2$	1,880	$C_5H_{12} + 8\ O_2$	2,371
$C_2H_6 + 3.5\ O_2$	2,363	$C_5H_{12} + 8\ O_2 + 24\ N_2$	1,680
$C_2H_4 + 3\ O_2$	2,209	$C_6H_6 + 7.5\ O_2$	2,206
$C_2H_4 + 2\ O_2 + 8\ N_2$	1,734	$C_6H_6 + 22.5\ O_2$	1,658
$C_2H_2 + 1.5\ O_2$	2,716	$C_2H_5OH + 3\ O_2$	2,356
$C_2H_2 + 1.5\ O_2 + N_2$	2,414	$C_2H_5OH + 3\ O_2 + 12\ N_2$	1,690

Liquid Burning Rates

Whereas burning velocities of combustible gases are relevant to explosion hazard evaluations, burning rates of combustible liquids—including liquefied gases—are important in assessing their fire hazards. The burning rate of a liquid pool is normally defined as a linear regression rate but can also be expressed as a mass or molar consumption rate per unit area. Data uncertainties are greatest for cryogenic fuels, which represent the extreme in vaporization rates.

Burgess (*7*) defined the liquid regression rates of various combustibles in ambient air as a function of pool diameter (fig. 56). With increasing pool diameter, the regression rates increase because of increased radiation feedback to the burning pool, resulting in greater vaporization and reaction. A pool diameter of about 1 m is required before the rates become maximum and level off for most of the fuels. Burgess gives the following expression for predicting the maximum burning rates:

$$v_\infty = 0.0076\ \Delta H_c/\Delta H_v, \qquad (74)$$

where v_∞ is the extrapolated rate at infinite pool diameter (cm/min) and $\Delta H_c/\Delta H_v$ is the ratio of net heat of combustion and sensible heat of vaporization (ΔH_v). For most hydrocarbon fuels, $\Delta H_c/\Delta H_v$ is about 100. This equation has been found to underestimate the burning rates of liquefied natural gas (LNG) in full-scale tests with 6-m-diam pools.

Table 21 (*7*) lists the calculated or experimental v_∞ values for various liquid fuels and the corresponding fractions of thermal energy that may be radiated in large-diameter pool fires. For hydrocarbon flames, the fraction of heat radiated to the surroundings can be expected to be between 25 and 40 pct, as compared to only 17 pct for methanol flames. Note that the burning rate of LNG is roughly comparable to that of butane, hexane, and gasoline. (See also figure 56.) The data for liquid hydrogen, which has by far the highest burning rate (1.4 cm/min), indicate that only about 25 pct of the thermal energy is radiated; however, these data are uncertain because of the limited range of testing. The special hazards associated with liquid hydrogen fires and explosions are summarized by Zabetakis (*111*).

Table 21. — Burning rates and radiative characteristics of burning liquid pools (*7*)

Combustible	Linear burning rates[1] (v_∞), cm/min	Thermal output		
		Total, kcal/(cm²·min)	Radiative	
			kcal/(cm²·min)	pct
n-Butane	0.79	5.1	1.4	28
n-Hexane	.73	5.1	2.0	39
Ethylene	NA	NA	NA	38
Benzene	.60	5.1	1.8	35
Xylene	.58	5.0	NA	NA
Gasoline	NA (~0.8)	NA	NA	NA
LNG	.66 (~0.9)	3.2	.8	25
Methanol	.17	.64	.11	17
Hydrogen	1.40	2.8	.7	25
UDMH	.38	2.2	.6	27

NA Not available.

[1]Computed rates for infinite diameter; parenthetical values from tests with 3-m diam pools.

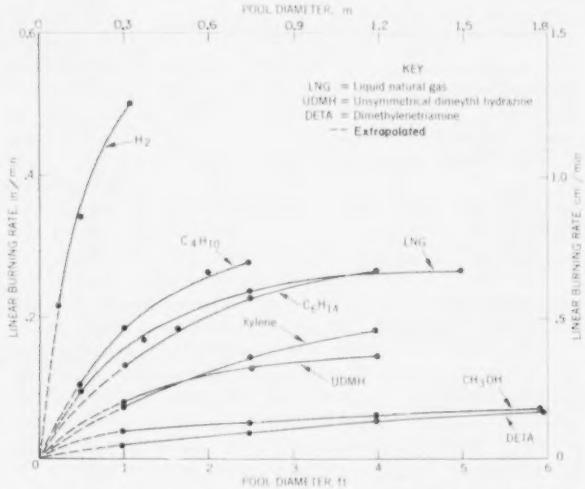


Figure 56.—Linear burning rates of combustible liquids as a function of pool diameter at ambient temperature.

PROPERTIES OF GASOLINES, JET FUELS, HYDRAULIC FLUIDS, AND LUBRICANTS

This section summarizes the combustion properties of composite liquid fuels, hydraulic fluids, and lubricating oils. Most of the data are derived from Bureau studies sponsored by the Air Force. Table 22 gives some of the common physical and combustion properties of various gasolines, diesels, and jet fuels. Table 23 gives corresponding combustion data for hydraulic fluids and lubricating oils. The flashpoints, minimum AIT's, and limits of flammability were determined by the same or modified methods previously described for the neat organic and inorganic combustibles.

Table 22. — Summary of combustion properties of gasolines, diesels, and jet fuels: Gaseous combustion in air at atmospheric pressure[1]

Fuel	Mol wt (av)	Sp gr (water = 1)	BP (90 pct), °C	C_{st}[2] (in air), vol pct	ΔH_c (net, 25° C)		Flash-point, °C	Minimum AIT, °C	Flammable limits	
					Btu/lb	cal/g			L_{25}, vol pct	U_{25}, vol pct
JP-1	151	0.81	210	1.3	18,480	10,265	46	230	NA	NA
JP-3	112	.76	227	(2.6)	18,710	10,395	NA	240	1.4	7.9
JP-4	125	.78	199	(2.4)	18,710	10,395	−18	240	1.3	8.2
JP-5	169	.83	238	1.1	18,440	10,245	66	225	[3]6	[3]4.5
JP-6	147	.84	260	(1.3)	18,620	10,345	38	230	[3]7	[3]4.8
JP-8	164	.8	238	NA	18,400	10,225	46	225	NA	NA
Jet A	NA	.8	249	NA	18,590	10,328	47	225	([4])	([4])
Jet B	NA	.8	199	NA	18,780	10,435	−7 to −18	230	([5])	([5])
Kerosene	NA	.8	254	(1.3)	18,600	10,335	52	230	[3]7	[3]4.8
Gasoline 100/130	NA	.7	116	(2.4)	19,000	10,555	−45	440	1.3	7.1
Gasoline 115/145	NA	.7	120	(2.2)	19,000	10,555	−45	470	1.2	7.1
Diesel fuel (60 cetane)	NA	.8	~325	NA	NA	NA	40 to 55	225	NA	NA

NA Not available.
[1]Flammability data from references 41-42, 47, and 114; physical property values are average or typical.
[2]Values in parentheses calculated by $C_{st} = L_{25}/0.55$.
[3]Values at 100° to 150° C.
[4]Similar to JP-5.
[5]Similar to JP-4.

Table 23. — Summary of combustion properties of hydraulic fluids and lubricating oils[1]

Fluid	Sp gr (water = 1)	Flash-point, °C	Fire point, °C	Minimum AIT, °C
MINERAL OILS				
MIL-H-5606 (oil)	0.9	90	107	225
MIL-2190 (oil)	.86	232	NA	350
MLO-60-294 (oil)	.88	196	221	370
Mobil DTE-103 (oil)	.92	199	NA	370
Pyrogard D (invert emulsion)	NA	NA	NA	~315
GLYCOLS				
Propylene glycol	NA	110	113	445
Houghto-Safe 271 (water-glycol)	1.05	NA	NA	410
Ucon 50 HB-260 (polyglycol)	1.04	235	260	395
PHOSPHATE ESTERS				
Cellulube 220 (ester base)	1.15	235	352	560
Skydrol (ester base)	NA	182	243	>700
Pydraul 150 (ester base)	1.13	193	243	525
Pydraul AC (ester base)	1.35	232	396	595
Houghto-Safe 1055 (aryl ester)	1.15	263	360	550
Tricresyl phosphate	1.17	243	NA	600
POLYOL AND DIBASIC ACID ESTERS				
MIL-L-7808 (acid diester)	NA	225	238	390
MIL-L-9236 (polyol ester)	NA	221	246	390
MLO-54-581 (acid diester)	NA	224	246	390
Plexol 201 (acid diester)	.91	216	232	~380
SILANES				
MLO-56-280 (diphenyl-dodecyl)	NA	291	329	415
MLO-56-610 (decyl-dodecyl)	NA	279	302	400
SILICATES AND SILICONES				
MLO-54-540 (silicate)	NA	163	221	375
MLO-54-856 (silicate)	NA	157	227	380
Oronite 8200 (silicate)	.93	196	227	380
Versilube F-50 (silicone)	1.05	288	338	480
Dow Corning 400 (siloxane)	NA	124	138	320
Dow Corning 500 (siloxane)	≤.95	243	NA	480
Dow Corning 550 (silicone)	1.07	316	NA	NA
CHLORINATED SILICONES AND HYDROCARBONS				
MLO-53-446 (silicone)	NA	304	377	420
Arachlor 1248 (diphenyl)	1.41	193	>315	~640
Pydraul A-200 (hydrocarbon)	1.42	177	360	650
AROMATIC ETHERS				
5P4E (polyphenoxy)	NA	293	349	610
OS-124 (polyphenyl)	1.20	288	349	600
MCS-293	1.19	220	270	490
MISCELLANEOUS FLUIDS				
SAE No. 10 lube oil	<1.0	171	193	380
SAE No. 60 lube oil	<1.0	249	327	380
Linseed oil	.95	224	279	440

NA Not available.
[1]Based upon data in references 47 and 52 and vendors' literature.

VAPOR PRESSURES AND FLASHPOINTS

Jet aircraft fuels can be classified as low- or high-volatility petroleum mixtures. The low-volatility grades are typically kerosenes, such as JP-1, JP-5, JP-6, and JP-8, which have a 10 pct boiling point of at least 177° C (350° F); commercial Jet A fuel also falls in this category. The high-volatility grades are blends of kerosene and high-octane aviation gasoline, such as JP-3 and JP-4, which have a 10 pct boiling point of about 110° C (230° F) or lower; commercial Jet B fuel and motor gasolines also fall in this category. In practice, the compositions of the different grades of fuels can vary with the sources and seasonal period of production. Their vapor compositions will necessarily depend upon the fractional distillation of the lighter ends that comprise such fuels.

Reid vapor pressure curves and flashpoint data are given for representative grades of aviation gasoline and five jet fuels in figure 57 (47). The Reid vapor pressures are normally determined at 38° C (100° F) and are slightly lower than true vapor pressures because the vapor-liquid ratio is not ideal in Reid determinations. The flashpoints are at least 38° C (100° F) for the low-volatility fuels and about −18° C (0° F) or less for high-volatility fuels. Diesel fuels fall in the flashpoint range of the low-volatility fuels. Thus, the vapors of the low-volatility fuels, including Jet A, which is used on most commercial passenger aircraft, will not form homogeneous flammable vapor-air mixtures at a normal ambient temperature of 20° C (68° F) and atmospheric pressure. However, flammable mists can form below the flashpoints of the liquids; see figure 6 and discussion. Assuming ideal behavior, the lower limit fuel concentrations at the flashpoint temperatures can be calculated from the vapor pressure data and equation 4. These may be compared to the experimental values given in table 22, which generally represent the limits of the completely vaporized fuels.

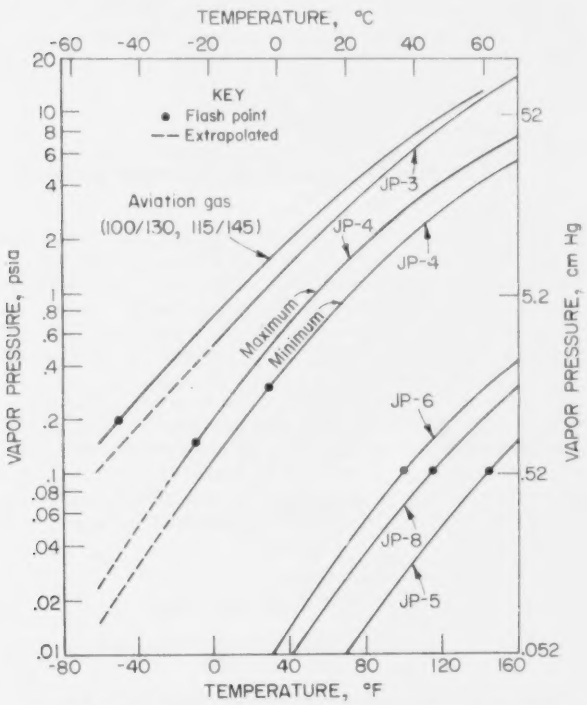


Figure 57.—Vapor pressure (Reid)-temperature curves and flashpoints for aviation gas and five jet fuels.

Both flashpoint and firepoint data are listed in table 23 for the hydraulic fluids and lubricating oils. The firepoint is the temperature at which flame can be sustained after the vapors have been ignited; differences between flashpoints and firepoints tend to be great for combustible liquids of low volatility and high fire resistance (high AIT). The flashpoints of hydraulic fluids and lubricating fluids are much higher than those of gasolines and jet fuels. Flashpoints of about 200° C or more are typical of the highly fire-resistant fluids for each chemical class of fluids. In the case of mineral-oil-based fluids, their flashpoints will be largely determined by the paraffinic and naphthenic constituents that are present; MIL-H-5606 oil, which has a flashpoint of only 90° C, is largely paraffinic and presents the greatest flammability hazard among these fluids. In the case of water-glycols, flashpoints will not exist until the excessive water has been removed. It is evident from these data that a high-temperature environment is required to realize a flashpoint hazard with the vapors of these fluids at normal pressure conditions.

FLAMMABILITY LIMITS IN AIR

Limits of flammability of completely vaporized fuel blends can differ from those obtained only with their lighter fractions, as in flashpoint determinations, since the limits vary inversely with the molecular weights of the combustible vapors. Data reported here are mainly those obtained with all fractions of the composite fuel present. As with flashpoint, the flammability limits of the gasolines and jet fuels in table 22 fall into two separate groups. The fuels of high volatility have a flammability range of approximately 1.3 (L_{25}) to 8 (U_{25}) vol pct or less in normal ambient air; those of low volatility have a limiting range of approximately 0.6 to 5 vol pct at ambient temperatures (100° or 150° C) above their flashpoints. These limits are comparable to those found for high-molecular-weight paraffins (>C_4) and the benzenes or naphthalenes (appendix A).

Bureau investigators have determined the flammability limits of aircraft-type fuels in air under various environmental conditions. Their data on the effects of mixture temperature and pressure for various gasolines and jet fuels are summarized in tables 24 and 25, respectively. Table 24 shows that the flammability limits of such fuel vapor-air mixtures on a weight basis vary only slightly with a moderate temperature increase; the lower limits at 25° C were at least 48 mg/L and the upper limits were at

Table 24. — Effect of temperature on flammability limits of gasolines and jet fuels in air at atmospheric pressure[1]

Fuel	Flammability limits, mg/L[2]			
	25° C		150° C	
	Lower	Upper	Lower	Upper
Av gas 100/130	56	350	53	348
Av gas 115/145	56	330	48	337
JP-1	NA	NA	48	380
JP-3	61	370	48	387
JP-4	48	330	47	330
JP-6	NA	NA	[3]46	290

NA Not available.
[1]Based upon data in references 41, 57, and 114.
[2]Mg fuel per liter of air at 0° C and at 1 atm.
[3]Data at 100° C.

Table 25. — Effect of pressure on flammability limits and minimum oxygen requirements for propagation of gasolines and jet fuels in air and air-inert mixtures at 25° C[1]

Fuel	Flammability limits, vol pct (in air)			Minimum oxygen, vol pct	
	Press, atm	Lower	Upper	Air-CO_2	Air-N_2
Motor gasolines[2]	1	1.4	7.6	14.9	12.1
Av gas 100/130	1	1.3	7.15	14.8	11.9
	.53	1.25	6.75	14.1	11.2
	.27	1.3	6.85	14.1	11.6
	.13	1.4	7.6	14.8	11.9
Av gas 115/145	1	1.2	7.1	14.6	11.9
	.53	1.25	6.9	14.6	11.6
	.27	1.25	7.0	14.8	11.6
	.13	1.5	7.85	14.9	12.0
JP-1	1	NA	NA	[3]13.9	[3]10.5
JP-3	1	1.45	7.95	14.3	11.8
JP-4	1	1.3	8.2	14.3([3]13.8)	11.5([3]10.9)
	.5	1.3	7.85	14.5	11.4
	.27	1.35	8.05	14.6	11.7
	.13	1.35	8.1	14.9	12.4

NA Not available.
[1]Based upon data in references 11, 41, and 42.
[2]73-100 octane ratings.
[3]Data at 150° C.

least 330 mg/L, which are consistent for fuels containing hydrocarbons. Conversion of weight concentration limits to volume percent can be made by equation 10; a fuel molecular weight of about 100 or more is a reasonable assumption for the vapors of these combustibles. Equations 63 and 64 may be used to estimate the volume concentration limits of these fuels at other temperatures. However, the AIT limitation on upper limit predictions cannot be neglected, as shown in figure 35 for the JP-6 fuel.

Pressure effects on the flammability limits of aircraft fuel vapor-air mixtures are similar to those observed for the neat hydrocarbons. Jones data (table 25) at 25° C showed little effect of reduced pressure down to nearly 1/10 atm or a pressure altitude of about 15 km (50,000 ft). Below such pressures, the ignition energy source becomes a serious limitation on flame propagation. At elevated pressures, the limits can be assumed to be widened similarly to that shown in figure 36 for hydrocarbon combustibles.

Meager flammability limit data are available for hydraulic fluids and lubricating oils. Although these fluids require rather high temperatures to form flammable vapor-air mixtures, their flammability limits can differ widely, depending upon the thermal stability and combustibility of the organic compounds that comprise the fluids. For example, the Oronite 8515 hydraulic fluid (silicate ester) is reported to have a lower limit of 64 mg/L, compared to 45 mg/L for the MIL-L-7808 engine oil (dibasic acid ester) in ambient air at 260° C (*52*). The lower limits of these fluids in air may be roughly estimated by use of equations 9 and 60 if the chemical formula of the fluid is known.

FLAMMABILITY LIMITS IN OTHER ATMOSPHERES

Jones and Zabetakis (*41-42, 114*) have published complete flammability diagrams for the vapors of various gasolines and jet fuels in air atmospheres diluted with nitrogen or carbon dioxide. Such flammability diagrams are shown in figure 58 for the highly volatile JP-4 fuel and in figure 7 for 100/130 grade aviation gasoline at 25° C and atmospheric pressure. A flammability diagram is also shown in figure 59 for the low-volatile JP-1 fuel at 150° C on a weight basis; the corresponding diagram for JP-4 did not differ greatly. Consistent with the data for hydrocarbons, the flammability limits are progressively narrowed with increased inert and more effectively with carbon dioxide than with nitrogen. For the fuels listed in table 25, the minimum oxygen concentrations required for flame propagation are 14 to 15 pct for air-CO_2 mixtures and 11.5 to 12 pct for air-N_2 mixtures at 25° C. Data in table 25 also indicate that the minimum oxygen values are lower at 150° C and are only slightly greater, if at all, at subatmospheric pressures to 0.13 atm. Such data are especially useful in evaluating the explosion hazard and inerting requirements of aircraft fuels in flight applications.

Inerting requirements for gasoline vapor-air mixtures are greatly reduced by the use of halogenated-type materials. The flammability diagram of figure 60 compares the effectiveness of various inerting agents for motor-type

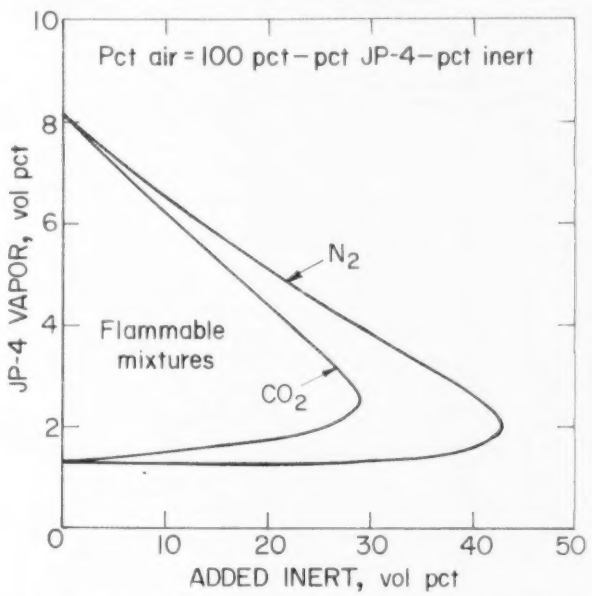


Figure 58.—Limits of flammability of JP-4 vapor-air-inert gas (CO_2 or N_2) mixtures at 25° C and 1 atm.

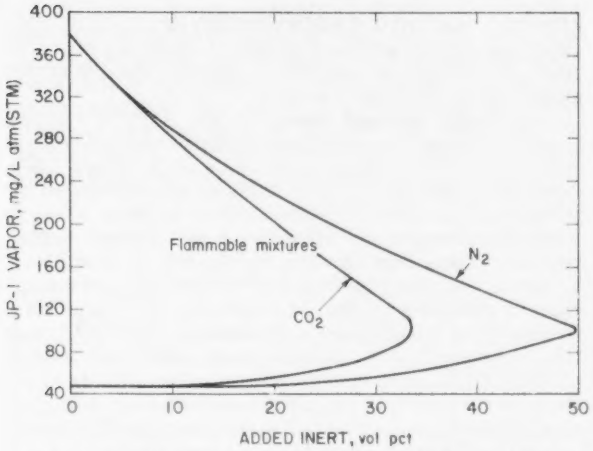


Figure 59.—Limits of flammability of JP-1 vapor-air-inert gas (CO_2 or N_2) mixtures at 150° C and 1 atm.

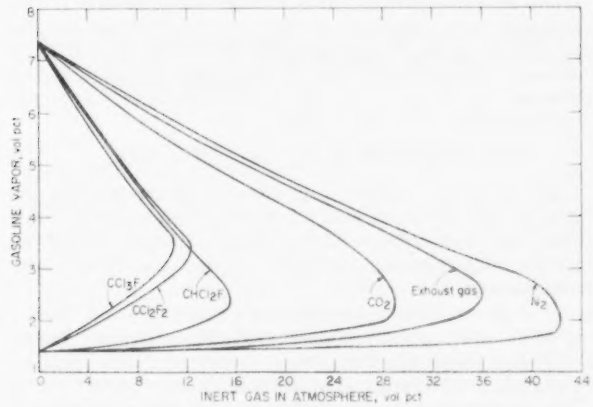


Figure 60.—Effects of various inerting agents on limits of flammability of gasoline vapor-air mixtures at 25° C and 1 atm.

gasolines (*11*); this figure represents the averaged data for motor gasolines of 73, 92, and 100 octane rating. Minimum oxygen values are 11.6 pct with nitrogen, 14.4 pct with carbon dioxide, and at least 17.2 pct with the halogenated methanes. Water vapor would be expected to be less effective than carbon dioxide and more effective than nitrogen or the exhaust gas (85 pct N_2 + 15 pct CO_2). Other inerting data for gasoline, kerosene, and JP-4 fuels are compared in table 12 with nitrogen, carbon dioxide, Halon 1211 (CF_2ClBr), and Halon 1301 (CF_3Br) as the inerting agents. As previously mentioned, the inerting requirements for premixed flames are not as severe as the extinguishing requirements for fully established fires of the same fuels.

IGNITION REQUIREMENTS

Ignition Energies

Few data are available on the precise determination of the minimum spark ignition energies of gasoline-type fuels. Nevertheless, since such fuels are comprised of hydrocarbons, the MIE values of their optimum vapor-air mixtures can be safely assumed to be about 0.2 to 0.3 mJ at 25° C and atmospheric pressure; note data of table 13. If the fuel is in the form of a fine spray or mist, the MIE will tend to be of the order of several millijoules, depending upon temperature (*48*). At temperatures greater than the flashpoint of the fuel, the spark ignition energies of the fuel sprays become drastically reduced and closer to that of the fuel vapor.

Ignition Temperatures

Autoignition temperatures of composite combustible liquids have been determined in heated vessels by the same procedures previously described for neat organic combustibles. As noted in table 22, minimum AIT's in quiescent air at atmospheric pressure are between 225° and 250° C for all the jet fuels and diesel fuels, whereas those for aviation gasolines are closer to 450° C. Although these combustibles contain a wide variety of hydrocarbons, their AIT variation may be compared to that observed for normal octane (220° C) and isooctane (415° C) or ethylcyclohexane (260° C) and ethylbenzene (430° C). The effect of chemical structure on AIT is also evident in comparing the data for the hydraulic fluids and lubricants (table 23). Those classified as aromatic ethers, phosphate esters, and chlorinated hydrocarbons have the highest AIT's, ~500° to 700° C; mineral oils have the lowest values, ~225° to 370° C, and depend greatly upon their paraffinic and naphthenic content; and glycols, silanes, silicates, ordinary silicones, and dibasic acid esters have intermediate values, ~350° to 475° C. Generally, the autoignition hazard for each chemical class is increased with the addition of aliphatic groups as opposed to aromatic groups.

The AIT's of aircraft liquid fuels, lubricants, and hydraulic fluids have been investigated by Zabetakis and coworkers under various environmental conditions. As with other combustibles, the minimum AIT's of the aircraft combustibles generally increase with decreasing pressure and oxygen concentration; such data are summarized in table 26 (*53, 113-114, 116*) for ignitions in air and oxygen.

Table 26. — Effect of pressure and oxygen concentration on the minimum AIT's of aircraft combustible fluids in oxygen-nitrogen atmospheres[1]

Combustible	Minimum AIT, °C			
	Air			Oxygen
	1/4 atm	1/2 atm	1 atm	1 atm
FUELS				
Kerosene	NA	NA	230	215
Av gas 100/130	NA	553	440	315
Av gas 115/145	NA	573	470	NA
JP-1	NA	462	228	NA
JP-3	NA	449	238	NA
JP-4	571	444	242	NA
JP-6	612	496	232	222
HYDRAULIC FLUIDS AND LUBRICANTS				
MIL-H-5606	556	438	225	220
MLO-53-446	442	424	419	408
MLO-54-540	510	448	373	230
MLO-54-581	548	480	390	274
MLO-54-645	520	452	380	256
MLO-54-856	516	460	380	266
MLO-8200	522	450	380	244
MIL-L-7808	NA	NA	402	270

NA Not available.
[1]Based upon data in references 53, 113-114, and 116.

The effect of reduced pressure on AIT's in air is greatest for the aircraft combustibles having the lowest AIT's at atmospheric pressure. Conversely, the effect of increased oxygen concentration is greatest for the combustibles of high AIT in normal atmospheric air. An exception is the MLO-53-446 chlorinated silicone hydraulic fluid, which was not sensitive to the above pressure and oxygen variations. Figure 61 (*116*) shows the oxygen effect on AIT for seven hydraulic fluids. Kuchta (*48*) found that the oxygen and pressure effects on AIT for jet fuels and lubricants or hydraulic fluids correlate well with the oxygen partial pressure of the atmosphere. Such a correlation is shown in figure 62 (*49*) for the JP-6 fuel in various oxygen-containing

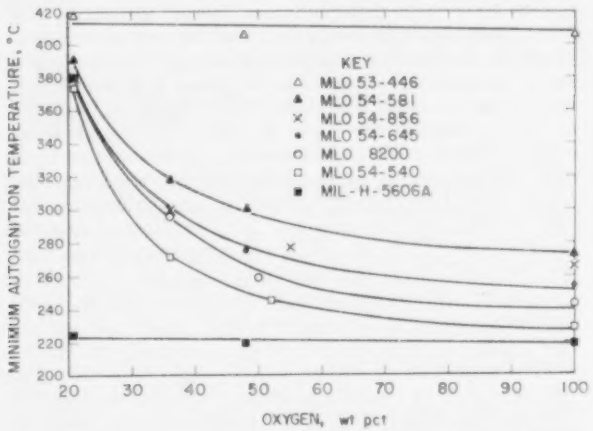


Figure 61.—Minimum autoignition temperatures of seven hydraulic fluids in oxygen-nitrogen mixtures at atmospheric pressure (glass vessels).

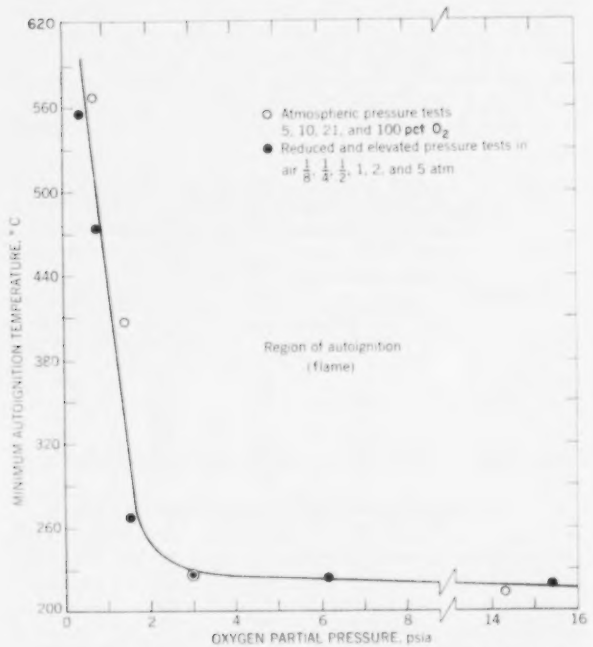

MINIMUM AUTOIGNITION TEMPERATURE, °C
OXYGEN PARTIAL PRESSURE, psia
Atmospheric pressure tests
5, 10, 21, and 100 pct O2
Reduced and elevated pressure tests in
air 1/8, 1/4, 1/2, 1, 2, and 5 atm
Region of autoignition
(flame)

Figure 62.—Correlation of minimum autoignition temperatures of JP-6 fuel-oxygen-nitrogen mixtures with oxygen partial pressure at various mixture pressures.

atmospheres at reduced and moderately elevated pressure. Below an oxygen partial pressure of about 0.2 atm (~3 psia), the AIT can be expected to increase sharply for organic fuels or fluids of this type.

At highly elevated pressures, the AIT's of aircraft fluids are noticeably lower than at 1 atm but tend to become constant. In figure 63 (*110*), the AIT's of phosphate ester, mineral oil, and water-glycol fluids in air are reduced by up to one-half with a pressure increase to about 100 atm; above this pressure, the AIT's varied only slightly. Similar pressure effects were observed for the MIL-L-7808, Mobil DTE-103, and Houghto-Safe-1055 lubricants in autoignitions at pressures to 1000 atmospheres (*48*); their AIT's (interpolated values) were approximately 200°, 230°, and 275° C, respectively, at 150 atm, above which they leveled off. The compression ignition hazard of these fluids in air can be assessed from such AIT data and adiabatic compression temperature data (table 5) at the pressures of interest.

All of the above-cited AIT data were obtained under static conditions with maximum contact times with the heated surface of the vessel. The much higher AIT's that can result with shorter contact times (ignition delays) are illustrated in figure 48; note data for JP-6, kerosene, and the petroleum fractions. A similar plot obtained for the JP-6 fuel in heated air streams at various pressures is shown in figure 64 (*57*); data in static air are also included. The AIT (T, K) variation with ignition delay (τ, ms) under flow conditions at 2 atm is given by

$$\text{JP-6 (370-600° C)} \quad \ln \tau = 5800/RT + 0.44, \qquad (74)$$

where R is in cal/(K·mol); in these experiments, the air velocity was between 6 and 50 m/s in a 5-cm-diam tube. With increasing pressure, the ignition delays at a given temperature decrease and, therefore, increase the autoignition hazard.

With small heated surfaces such as wires or rods, the ignition temperatures are also higher than heated vessel AIT's and follow the data trends displayed by JP-6 jet fuel and MIL-L-7808 engine oil in table 16 and figure 49 (*50*). The wire ignition temperatures (T, °C) of such aircraft combustibles in air under near-stagnant conditions are given by the following expressions as a function of the heat source surface area (A, cm^2):

$$\text{JP-6} \qquad T = 985 - 112 \ln A;\ A < 80\ cm^2 \qquad (75)$$

$$\text{MIL-L-7808} \qquad T = 752 - 64 \ln A;\ A < 190\ cm^2 \qquad (76)$$

or in terms of radius of the heat source (r, cm):

$$\text{JP-6} \qquad \ln r = 12{,}000/T - 12.9;\ r < 0.7\ cm \qquad (77)$$

$$\text{MIL-L-7808} \qquad \ln r = 14{,}000/T - 17.7;\ r < 1.3\ cm \qquad (78)$$

where T is in K. These data indicate the importance of the heat source dimensions in comparing ignition temperatures. So-called hot manifold or hotplate ignition temperatures are also higher than vessel AIT's, depending upon the size of the heated surface and the flow or convective conditions that determine the contact time. For jet fuels and the MIL-H-5606 fluid, the hotplate-type ignition temperatures tend to be about double their vessel AIT's in quiescent air. Reference 48 summarizes these and other ignition properties of jet fuels and various aircraft fluids.

Ignitions of fuels and lubricants by jets of hot gases are not common but can occur as a result of seal failures or pinhole leaks in pressurized systems. They are also of interest in designing flame arrestors and explosionproof equipment. Ignition temperature data obtained with hot

air jets for the JP-6 fuel and MIL-L-7808 oil (*51*) have been replotted in figure 65, together with wire and vessel ignition temperatures, as a function of heat source diameters. As with neat hydrocarbons, the highest ignition temperatures occur with the hot air jets, depending upon their diameter; see also table 16. The fact that vessel AIT's become greater than wire ignition temperatures at small heat source diameters is due to increased wall quenching.

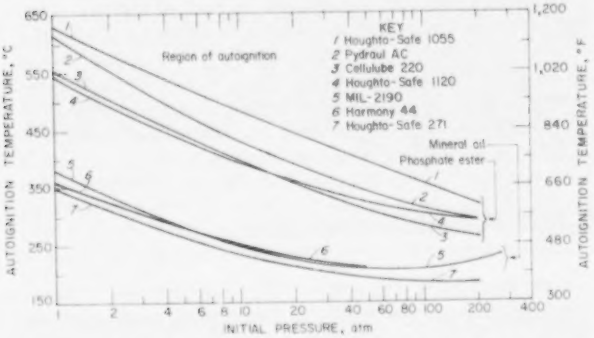


Figure 63.—Minimum autoignition temperatures of phosphate ester, mineral oil, and water-glycol hydraulic fluids or lubricants in air at elevated pressures.

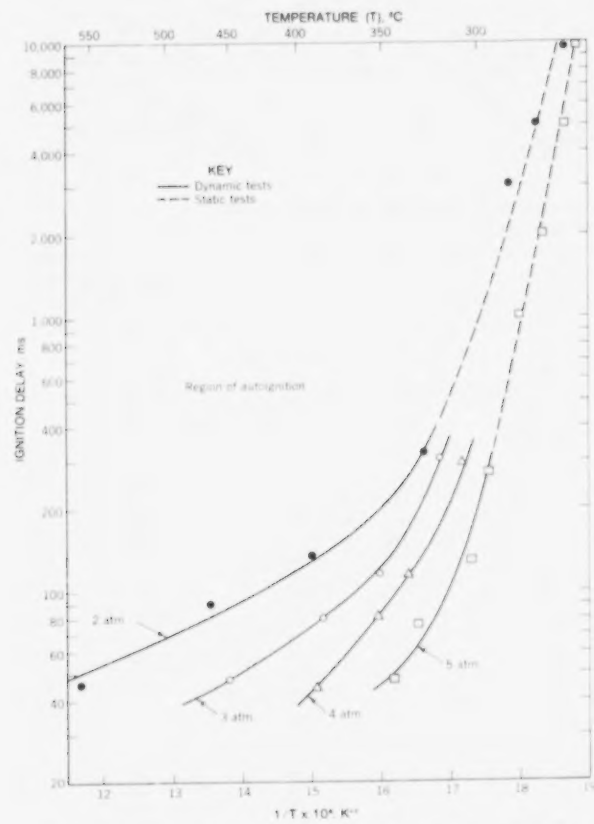


Figure 64.—Autoignition temperatures and corresponding ignition delays for JP-6 fuel under static and dynamic conditions in air at various pressures.

FLAME TEMPERATURES AND BURNING RATES

Flame Temperatures

Maximum flame temperatures of the optimum vapor-air mixtures of petroleum-derivable combustibles can be assumed to be comparable to those of the neat hydrocarbons, 1,900° to 2,000° C (table 17). Similarly, their limit

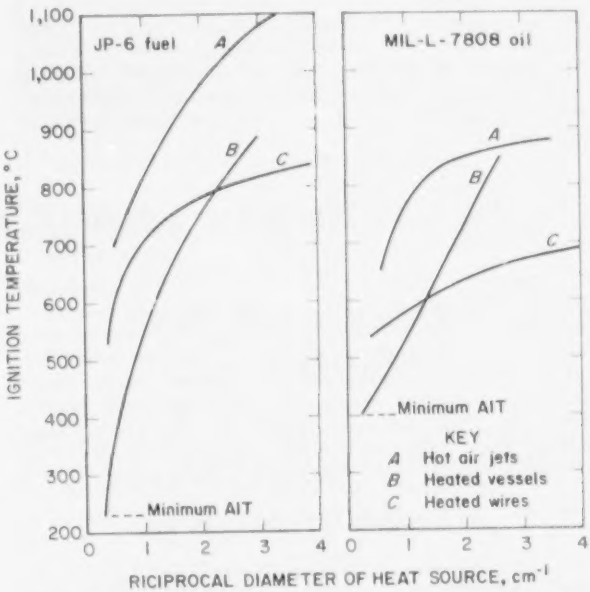


Figure 65.—Variation of hot gas (air) and hot surface ignition temperatures with reciprocal diameter of heat source for JP-6 fuel and MIL-L-7808 oil vapor-air mixtures at atmospheric pressure.

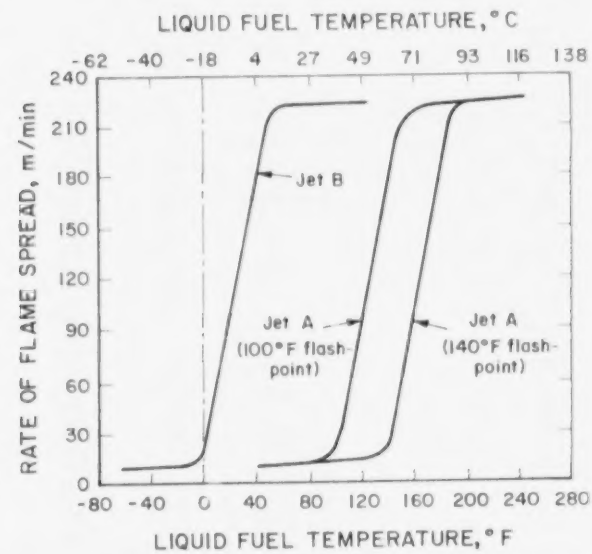


Figure 66.—Flame spread rate versus liquid fuel temperature for Jet A- and Jet B-type fuels in air at atmospheric pressure.

flame temperatures should be in the 1,200° to 1,300° C range. Such flame temperature estimates are fairly reliable for gasolines, jet fuels, and the mineral oil hydraulic fluids.

Burning Rates

The liquid burning rates (regression rates) of petroleum-based fuels are necessarily dependent upon the size of the burning pool. At an infinite pool diameter, the rate for a gasoline-type fuel should be about 0.6 to 0.8 cm/min (table 21). For smaller pools, the rates for xylene in figure 56 are most relevant for the gasoline or jet fuels. This figure also indicates that higher rates will occur for fuels containing higher concentrations of low-molecular-weight paraffins. The burning rates may be estimated by equation 74.

Flame spread rates of liquid fuels are strongly dependent upon their volatility or flashpoint. Figure 66 (*47*) shows the reported variation of flame spread rate (horizontal) with fuel temperature for Jet A and Jet B-type fuels. It is important to note that the flame spread rates increase drastically when the fuel temperature is above the flashpoint of the given fuel. Also, the maximum rates are of the order of flame speeds (~10 ft/s) encountered with premixed hydrocarbon vapor-air systems. The indicated maximum rates can be realized in real situations when the liquid fuel is heated substantially above its flashpoint, or when it is finely dispersed to produce flash vaporization, as in an aircraft crash situation. The rates are also enhanced when the fuel is in the form of a thin liquid film. Much higher rates than those in figure 66 are possible under windy conditions.

PROPERTIES OF METAL AND NONMETAL ELEMENTS

Physical properties of elemental metals and nonmetals are given in table 27 together with ignition temperature and explosion limit (flammability limit) data for the combustion of their dusts. The dust combustion data were taken from the comprehensive compilations by Nagy, Jacobson, and other Bureau coworkers but were limited primarily to the elemental substances of relatively high purity. Their data for various combustibles are conveniently summarized in an NFPA handbook (*72*).

FLAMMABILITY LIMITS IN AIR

Lower explosion limits of the dusts in table 27 (*36, 76*) were determined in normal ambient air by the widely known Hartmann apparatus (*13*), equipped with a 7-cm-diam explosion tube (1.23 L) and a high-voltage spark source (~24 W) for ignition. A dust particle size of less than 74 μm (minus 200 mesh) was used to obtain most of these limits. These data show that a dust explosion hazard may arise with a wide variety of metallic or nonmetallic elements, including aluminum, tin, iron, zinc, and silicon. Aluminum, magnesium, titanium, and sulfur are among the widely used substances having a relatively low dust explosion limit, less than 0.1 g/L or 0.1 oz/ft^3. In comparison, the dusts of such elemental substances as carbon and copper could not be ignited under the given conditions. Because of apparatus limitations, including the lack of uniform dust dispersions, the reported limits cannot be

Table 27. — Summary of combustion properties of elemental metal and nonmetal dusts: Dust combustion in air at atmospheric pressure[1]

Combustible	At wt	Density, g/cm^3	MP, °C	ΔH_f° (25° C), kcal/mol	Ignition temperature[2]		Lower explosion[3] limit (L_{50}), g/L
					Layer, °C	Cloud, °C	
Aluminum, atomized	26.98	2.70	660	199.5 (Al_2O_3)	490	670	0.075
Antimony (96 pct), milled	121.75	6.68	631	83.3 (Sb_2O_3)	330	420	420
Barium	137.34	3.51	725	133.0 (BaO)	NA	NA	NA
Boron (85 pct), amorphous	10.82	2.32	2,300	151.0 (B_2O_3)	400	470	>100
Cadmium (98 pct), atomized	112.40	8.64	321	60.9 (CdO)	250	570	NI
Carbon, lampblack	12.01	2.27	>3,500	94.1 (CO_2)	NA	730	NI
Chromium (97 pct), milled	52.00	7.20	1,857	134.9 (Cr_2O_3)	400	580	230
Cobalt (97.8 pct), milled	58.93	8.90	1,495	57.2 (CoO)	370	760	NI
Copper (99.5 pct), electrolytic	63.55	8.92	1,083	37.1 (CuO)	NA	700	NI
Iron (98 pct)	55.85	7.86	1,535	98.3 (Fe_2O_3)	290	320	120
Lead (99 pct), atomized	207.20	11.34	328	52.4 (PbO)	270	710	NI
Lithium	6.94	53	181	71.2 (Li_2O)	NA	NA	NA
Magnesium, milled	24.31	1.74	649	143.8 (MgO)	430	560	030
Manganese	54.94	7.20	1,244	124.5 (MnO_2)	240	460	125
Molybdenum (99.8 pct)	95.94	10.20	2,617	180.3 (MoO_3)	360	720	NI
Nickel	58.71	8.90	1,453	58.4 (NiO)	NA	NA	NA
Phosphorus, white	30.97	1.83	44	180.0 (P_2O_5)	NA	NA	NA
Potassium	39.10	86	64	43.2 (K_2O)	NA	NA	NA
Silicon (96 pct), milled	28.06	2.40	1,420	205.4 (SiO_2)	950	780	160
Sodium	22.99	97	98	49.7 (Na_2O)	NA	NA	NA
Sulfur	32.06	2.0	113	71.0 (SO_3)	220	190	035
Tantalum	180.95	14.0	300	250.0 (Ta_2O_5)	300	630	>200
Thorium (1.2 pct O_2)	232.04	11.70	1,750	292.0 (ThO_2)	280	270	075
Tin (96 pct), atomized	118.69	5.0	232	138.8 (SnO_2)	430	630	190
Titanium (99 pct)	47.90	4.5	1,660	183.5 (Ti_2O_3)	510	330	045
Tungsten	183.85	19.35	3,410	136.3 (WO_3)	430	NA	NI
Uranium	238.03	19.05	1,132	250.0 (UO_2)	100	20	060
Vanadium (86.4 pct)	50.94	5.96	1,890	145.0 (V_2O_5)	490	500	220
Zinc (97 pct)	65.38	7.14	420	83.2 (ZnO)	540	690	480
Zirconium (97 pct)	91.22	6.49	1,852	258.2 (ZrO_2)	20	190	045

NA Not available. NI No ignition with electric spark source.

[1] Flammability data from references [illegible].

[2] Values calculated from ΔH_f (25° C) data [illegible] reference 105.

[3] Combustible particle size less than 74 μm (200 mesh); g/L equates to oz/ft^3.

assumed as absolute. Sample purity itself can have a large effect on these limits.

The ignition and explosion parameters of dusts are strongly dependent upon their particle size. Figure 67 (*36*) shows the effect of average particle diameter on the lower explosion limit and other parameters for atomized aluminum-air mixtures in the Hartmann apparatus; the minus 200-mesh data in table 27 would correspond to those for a 30-μm average particle diameter. Note that the explosion limit increases greatly when the average particle diameter is greater than approximately 50 μm. Also, the maximum explosion pressures are not any greater than those previously cited for organic combustible vapor-air mixtures. However, dusts do not necessarily have well-defined upper flammability limits and are capable of high explosion pressures even with highly fuel-rich mixtures. Data by the above authors indicate that, for most metals, dust concentrations of 1 to 2 g/L (1 to 2 oz/ft^3) are required to achieve near-maximum explosion pressures in an air atmosphere. With increasing ignition energies, the range of possible explosive concentrations will tend to widen.

Table 28. — Inerting requirements to prevent propagation of elemental metal and nonmetal dusts in air-nitrogen, air-carbon dioxide, and air-inert dust (fuller's earth) mixtures (spark ignition) (*77*)

Combustible	Lower explosion limit $(L_{25})_3$ kg/m^3	Minimum oxygen limit, vol pct		Minimum inert dust limit, wt pct
		Air-N_2	Air-CO_2	
Aluminum, atomized, <74 μm	0.075	9	3	80
Aluminum, atomized, <44 μm	.045	NA	2	90
Iron, 98 pct, <53 μm	.12	NA	11	50
Magnesium, milled, <74 μm	.03	2	[1]<1	90
Silicon, 98 pct, milled, < 74 μm	.11	11	12	70
Sulfur, 99 pct, <44 μm	.035	NA	12	85
Tin, 96 pct, atomized, <53 μm	.19	NA	16	30
Titanium, 96 pct, < 44 μm	.045	4	[1]<1	85
Zinc, 95 pct, <74 μ	.50	10	10	35
Zirconium, 97 pct, <44 μm	.045	2	[1]<1	90 +

NA Not available.
[1]Reported ignitions with only diluent present.

FLAMMABILITY LIMITS IN OTHER ATMOSPHERES

Explosion limits of the elemental dusts are narrowed by the reduction of oxygen concentration, addition of inert gas, or addition of inert dust. Table 28 summarizes some explosion inerting data from the Bureau studies (*77*) for the dusts of several metals or nonmetals in normal air at atmospheric pressure; these data apply to electrical spark ignitions. With an inert dust of fuller's earth of less than 74 μm (minus 200 mesh) or 44 μm (minus 325 mesh), the more reactive substances require about 80 wt pct or more of inert to prevent an explosion; only 30 to 50 pct inert dust is required for the much less reactive substances. Gaseous inerts are not any more effective in preventing their explosions. For the more reactive metal dusts, the critical oxygen concentrations in air-CO_2 atmospheres extend down to less than 1 vol pct; note that the magnesium, titanium, and zirconium dusts ignited in the diluent alone. Corresponding minimum O_2 values in air-N_2 atmospheres tend to be higher than those for air-CO_2 atmospheres for these materials. With all such dusts, the inerting requirements will vary with their particle size and purity or contamination.

IGNITION REQUIREMENTS

Ignition Energies

Available ignition energy data for combustible dusts are not as precisely defined as those for combustible gases because of great experimental uncertainties. Nevertheless, the reported data in the above cited works provide a relative estimate of the spark ignition energy requirements for various dusts. The minimum ignition energies of dust-air clouds are one or more orders of magnitude greater than those of combustible gas-air mixtures, depending greatly upon the dust particle size. Figure 67 includes the variation of minimum spark ignition energy with average particle diameter for an atomized aluminum dust cloud. For metal dusts of minus 200 mesh (<74 μm), the minimum ignition energies are as low as several millijoules for the most reactive metals and as high as several joules for the least reactive ones; those of moderate reactivity have values mostly of about 100 mJ or more.

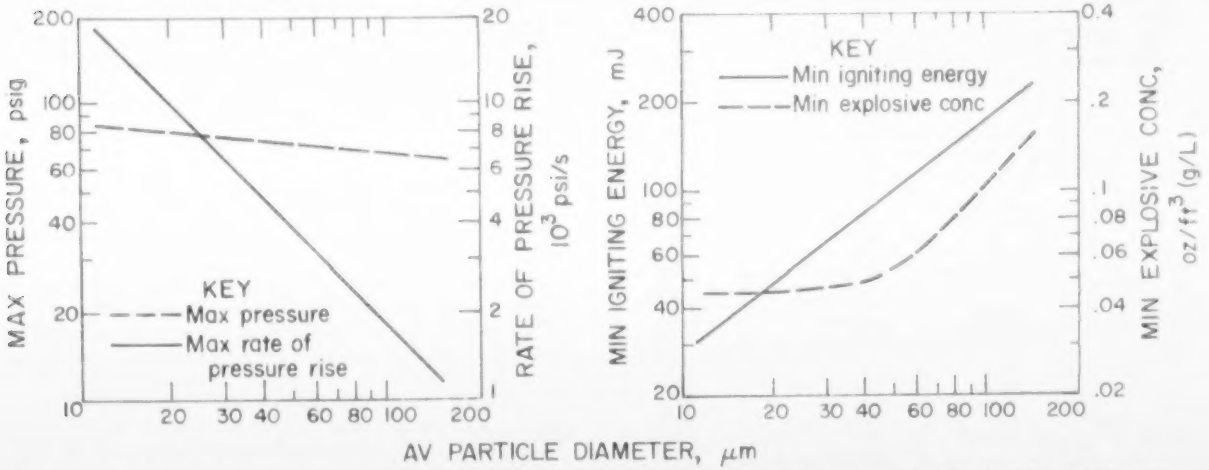


Figure 67.—Effect of average particle diameter on explosion parameters for atomized aluminum dust in air at 25° C and 1 atm.

Ignition Temperatures

The dust ignition temperatures given in table 27 were determined largely by Jacobson (*36*) using the Godbert-Greenwald apparatus, 3.65-cm-diam furnace. As noted, ignition temperatures of the metallic and nonmetallic dusts in air are generally lower when the heated dust is a layered mass, as opposed to a dispersed mass (cloud); most obvious exceptions are titanium and uranium. Most of these ignition temperatures were obtained with dusts of less than 74 μm (minus 200 mesh) but do not necessarily represent the lowest possible ignition temperatures for finer size dusts or for large dust layers that approximate adiabatic conditions. The most temperature sensitive materials are those that can undergo pyrophoric reaction at room temperature; these include uranium, zirconium, sodium, potassium, lithium, and white phosphorus. Their reaction is normally enhanced by increased humidity.

Metals in bulk form are much more difficult to ignite than those that are finely divided and, therefore, their ignition temperatures are usually found in an oxygen-enriched atmosphere. Ignition temperatures of metals in oxygen are given in table 29 (*29, 62*) with samples in rod or block form that have been preheated in oxygen or argon. Although all data are not consistent, the ignition temperatures tend to be near or above the melting point of the pure metal; also, most values are higher when the metals are preheated in oxygen, rather than an inert gas (argon). The oxygen preheating reflects the effect of the formation of metal oxides on the surface, thereby making ignition usually more difficult because of higher melting points and lower reactivities of the oxide coatings. This effect is least for metals of low melting point or for metals whose oxides are of similar or lower melting point.

FLAME TEMPERATURES AND BURNING RATES

Flame Temperatures

Maximum flame (or combustion) temperatures of metals and nonmetals are difficult to calculate precisely because the oxide species may be uncertain at the high temperatures and because thermodynamic data may be unavailable. Table 30 lists the calculated adiabatic temperatures by Grosse (*29*) for the combustion of such substances in an atmosphere of oxygen. These temperatures are necessarily above the melting point and boiling points of the oxides that may be formed by the elemental substances. Also, the values are roughly consistent with the variation of the molar heats of combustion (table 27) of the elements. As with hydrocarbons, the combustion temperatures are greatly reduced by any dissociation of the reaction products; the high heat capacities of metal oxides are also a contributing factor.

Table 29. — Ignition temperatures of bulk metals in oxygen at atmospheric pressure (metal sample in rod or block form) (*29,62*)

Metal	Melting point, °C		Metal ignition temperatures, °C	
	Metal	Oxide	Preheated in oxygen (*62*)	Preheated in argon (*29*)
Aluminum	660	2,045 (Al_2O_3)	NA	>1,000
Antimony	631	656 (Sb_2O_3)	NA	720
Barium	725	1,923 (BaO)	550	175
Bismuth	271	820 (Bi_2O_3)	735	775
Cadmium	321	[1]900 (CdO)	NA	760
Calcium	839	2,580 (CaO)	790	550
Iron	1,535	1,565 (Fe_2O_3)	1,315	930
Lead	328	888 (PbO)	850	870
Lithium	181	>1,700 (Li_2O)	NA	190
Magnesium	649	2,800 (MgO)	635	625
Molybdenum	2,617	795 (MoO_3)	780	750
Potassium	64	[1]350 (K_2O)	NA	69
Sodium	98	460 (Na_2O)	NA	118
Strontium	769	2,430 (SrO)	1,075	720
Thorium	1,750	3,050 (ThO_2)	NA	500
Tin	232	1,127 (SnO_2)	940	865
Zinc	420	1,975 (ZnO)	905	900

NA Not available.
[1]Decomposition.

Table 30. — Adiabatic combustion temperatures of metals and nonmetals in oxygen at 1 atm (*29*)

Substance	Adiabatic combustion temperature, K	Substance	Adiabatic combustion temperature, K
Aluminum	3,800	Magnesium	3,350
Antimony	1,700	Manganese	3,400
Barium	3,000	Molybdenum	3,000
Beryllium	4,300	Potassium	1,700
Bismuth	2,000	Silicon	2,500
Boron	2,900	Sodium	2,000
Cadmium	1,700	Strontium	3,500
Calcium	3,800	Thorium	4,700
Iron	3,000	Tin	2,700
Lead	1,800	Titanium	3,300
Lithium	2,600	Zinc	2,200
		Zirconium	4,800

Burning Rates

The burning rates of granular combustibles are usually determined in the horizontal burning mode, although both rates of consumption and flame spread are greater in the upward burning mode. Most of the available data for elemental metals or nonmetals are limited to substances that are readily ignitable. Bureau investigators (*60*) reported horizontal burning rates in air of about 200 cm/min for such granular materials as titanium and phosphorus (red) of 100 to 200 mesh; in comparison, the rates for magnesium ranged from 2 to 75 cm/min, depending upon the dust particle size. For comparison with other flammable solids, these data are included in the burning rate tabulations of the next section for various industrial dusts.

PROPERTIES OF AGRICULTURAL, CARBONACEOUS, CHEMICAL, AND PLASTIC DUSTS

This section covers combustion properties of various industrial dusts that are classified as agricultural, carbonaceous, chemical, and plastic types. Coal, which is a carbonaceous material, is given special emphasis because of the high fire or explosion risks in the coal mining industry and because of the great usefulness of the many mine safety data that have been generated. Table 31 summarizes selected ignition and flammability data that were obtained

Table 31. — Summary of combustion properties of agricultural carbonaceous, chemical, and plastic dusts[1]

Combustible	Ignition temperature		Lower explosion limit (L_{25}),[2] g/L
	Layer, °C	Cloud, °C	
AGRICULTURAL DUSTS			
Alfalfa meal	NA	530	0.105
Cellulose	270	480	.055
Cereal grass	230	620	.20
Corn	250	400	.055
Cornstarch (minus 325-mesh)	350	390	.04
Cotton linter, raw	NA	520	.50
Cottonseed meal	310	540	.055
Grain (wheat, corn, oats, barley)	230	430	.055
Gum, arabic	260	500	.06
Lycopodium	310	480	.025
Pea flour	260	560	.05
Potato starch, dextrinated	NA	440	.045
Rice	450	510	.085
Soybean meal	340	550	.06
Sucrose	400	370	.045
Tobacco stem	230	420	NI
Wheat, untreated	220	500	.065
Wood, birch bark	250	450	.020
Wood flour, white pine	260	470	.035
CARBONACEOUS DUSTS			
Asphalt, brown petroleum resin	500	510	0.025
Carbon, activated, petroleum sludge	490	760	NI
Carbon black, acetylene	900	NA	NI
Charcoal, activated, lignite	370	670	2.00
Charcoal, hardwood mixture	180	530	.14
Coke, bituminous coal	440	710	NI
Coke, petroleum	NA	670	1.00
Gilsonite, Utah	500	580	.02
Oil shale (17 gal/ton), Colorado	350	440	NI
Oil shale (10 gal/ton), Tennessee	260	630	NI
Pitch, coal tar	NA	650	.045
Pitch, petroleum	NA	630	.045
Coal, lignite, California	200	450	.03
Coal, lignite, North Dakota	180	440	.045
Coal, bituminous, Fox Hill, CO	180	440	.045
Coal, bituminous, No. 7, Illinois	160	600	.04
Coal, bituminous, Whitesburg, KY	190	595	.05
Coal, bituminous, Bruceton, PA	170	610	.055
Coal, bituminous, Pocahontas No. 3, West Virginia	220	640	NI
Coal, bituminous, Laramie No. 3, Wyoming	180	575	.04
CHEMICAL DUSTS			
Acetoacetanilide	NA	560	0.03
Adipic acid	NA	550	.035
Anthranilic acid	NA	580	.03
Azealic acid	NA	610	.025
Benzoic acid	NA	620	.03
Benzotriazole	NA	440	.03
o-Chloroacetoacetanilide	NA	640	.035
Dehydroacetic acid	NA	430	.03
Diallyl phthalate	NA	480	.03
Dimethyl isophthalate	NA	580	.025
Dimethyl terephthalate	NA	570	.03
3,5-Dinitrobenzoic acid	NA	460	.05
Diphenyl	NA	630	.015
Ethyl hydroxyethyl cellulose	NA	390	.02
Fumaric acid	NA	520	.085
Hexamethylenetetramine	NA	410	.015
Hydroxyethyl cellulose	NA	410	.025
Isatoic anhydride	NA	700	.035
Nitrosoamine	NA	270	.025
Paraformaldehyde	NA	410	.04
Paraoxybenzaldehyde	430	380	.02
Paraphenylenediamine	NA	620	.025
Pentaerythritol	NA	450	.03
Phthalic anhydride	NA	650	.015
Phthalimide	NA	630	.03
Salicylanilide	NA	610	.04
Sorbic acid	460	470	.02
Stearic acid, aluminum salt	440	420	.015
Stearic acid, zinc salt	NA	510	.02
Sulfur	220	190	.035
Terephthalic acid	NA	680	.05

Table 31. — Summary of combustion properties of agricultural carbonaceous, chemical, and plastic dusts[1] — Continued

Combustible	Ignition temperature		Lower explosion limit (L_{25}),[2] g/L
	Layer, °C	Cloud, °C	
PLASTIC DUSTS (RESINS AND MOLDING COMPOUNDS)			
Acetal, linear, polyformaldehyde	NA	440	0.035
Acrylamide polymer	NA	480	.03
Acrylonitrile polymer	460	500	.025
Cellulose acetate	NA	420	.04
Cellulose triacetate	NA	430	.04
Cellulose propionate (0.3 pct free hydroxyl)	NA	460	.025
Epoxy (no catalyst or additives)	NA	540	.02
Ethyl cellulose (5- to 10-μm)	350	370	.025
Ethylene-maleic anhydride copolymer	NA	540	.095
Ethylene oxide polymer	NA	350	.03
Melamine formaldehyde, laminating type	NA	790	.065
Methyl cellulose	340	360	.03
Methyl methacrylate, polymer	NA	440	.035
Phenol formaldehyde, 1-step	NA	640	.04
Phenol formaldehyde, 2-step	NA	580	.025
Phenol furfural	NA	530	.025
Polycarbonate	NA	710	.025
Polyethylene, high-pressure process	380	450	.02
Polyethylene wax, low-molecular weight	NA	400	.02
Polymethylene, carboxy	NA	520	.325
Polypropylene (no antioxidant)	NA	420	.02
Polystyrene, clear	NA	490	.02
Polyurethane foam, non-fire-retardant	440	510	.03
Polyurethane foam, fire-retardant	390	550	.025
Polyvinyl acetate	NA	550	.04
Polyvinyl acetate alcohol	440	520	.035
Polyvinyl butyral	NA	390	.02
Polyvinyl chloride, fine	400	660	NI
Styrene-butadiene latex	NA	440	.025
Urea formaldehyde molding compound	NA	460	.085
Vinylidene chloride molding compound	NA	900	NI
OTHER DUSTS			
Nylon, polyamide	430	500	0.03
Rayon flock, viscose	250	520	.055
Rosin, DK	NA	390	.015
Rubber, crude, hard	NA	350	.025
Rubber, synthetic, hard (33 pct S)	NA	320	.03
Rubber, chlorinated	290	940	NI
Shellac	NA	400	.02

NA Not available NI No ignition with electric spark source.
[1]Flammability data from references 14, 37-38, and 76.
[2]Combustible particle size less than 74 μm (−200 mesh); g/L equates to oz/ft³.

by Nagy, Jacobson, and coworkers (*14, 37-38, 76*) for the various classes of combustible dusts in a normal ambient air atmosphere.

FLAMMABILITY LIMITS IN AIR

It is evident from tables 31 and 27 that practically all industrial dusts are capable of forming flammable dust-air mixtures. The table 31 data were also obtained with the previously described Hartmann apparatus (1.23 L) and spark ignition source using largely particle size dusts of less than 74 μm (minus 200 mesh). With some exceptions, particularly among carbonaceous dusts, the lower explosion limits (L_{25}) of the various classes of dusts are less than 0.06 g/L (0.06 oz/ft³). Many of the chemical and plastic dusts have lower limits as low as 0.02 or 0.03 g/L. Because the dust dispersions in this apparatus were not uniform, the assumed concentration limits in tables 27 and 31 should be regarded as nominal values. As with metal dusts, the organic combustible dusts have no well-defined upper limits.

The lower explosion limits of high-volatile bituminous coal dusts are 0.04 to 0.06 g/L in air by the above spark ignition method. Recent work by Hertzberg (*31*) with a modified Hartmann apparatus—larger volume (8 L), stronger ignition source, and more uniform dust dispersion—yielded limit values that were 2 or more times greater for such coals. They reported a limit of 0.135 g/L for Pittsburgh (Bruceton) coal dust of minus 200 mesh using electrical match ignition energies of the order of 200 J. This dust concentration was verified by optical measurements, whereas the earlier values represent gross concentrations derived from the mass loadings that were dispersed. Nevertheless, full-scale experiments in the Bruceton Experimental Mine indicate explosions can occur with a Pittsburgh coal dust loading of 0.049 g/L or more (*90*). Thus, the limit data in table 31, which were obtained by the standard Hartmann apparatus, are not overly conservative for safety purposes.

The lower limits of carbonaceous dust-air mixtures decrease greatly with increased volatility of the dust or increased methane content of the atmosphere. *Figure 68* shows such data for the high-volatile (−35 pct) Pittsburgh coal, low-volatile (−16 pct) Pocahontas coal, and an oil shale assayed at 45 gal/ton. These data were reported by Richmond (*90*) and refer to electrical match ignitions in the modified Hartmann apparatus. With the standard apparatus and spark ignition source, the Pocahontas coal and most coals of lower volatility gave ignitions in oxygen but not in air (*76*). For the more volatile coals given in table 31, their lower explosion limits in oxygen were at least 1/2 lower than their listed values in air. Anthracite coal dusts also do not ignite in air with ordinary electrical spark sources.

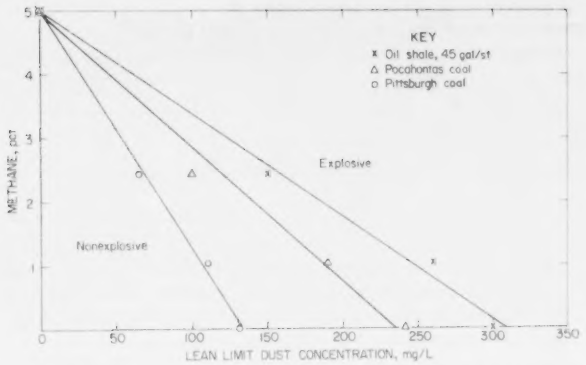


Figure 68.—Lower dust explosion limits of oil shale (45 gal/ton), Pocahontas coal, and Pittsburgh coal in methane-air atmospheres with modified Hartmann apparatus.

FLAMMABILITY LIMITS IN OTHER ATMOSPHERES

Selected inerting data for the various classes of organic industrial dusts are given in table 32. These data were obtained by Nagy and other Bureau investigators in electrical spark ignition experiments with near-optimum concentrations of the dispersed dusts in air; dust particle size was nominally less than 74 μm. With CO_2 as the inert, the minimum oxygen values to prevent propagation ranged from 11 to 18 pct. The values for cornstarch, acetal resin, and methyl methacrylate dusts were lowest (11 pct), and those for carbonaceous dusts were consistently highest (15 to 18 pct). The data with N_2 as the inert are meager but clearly indicate the smaller effectiveness of this agent. Similar to the lower limits, the minimum oxygen values are greatly dependent upon the volatiles and pyrolysis products that can be formed by the combustible dusts.

Dust explosions can also be prevented by adding a dry powder inert or inhibitor to the combustible dust. With an inert such as calcined fuller's earth, the above Bureau investigators found that except for melamine formaldehyde at least 60 wt pct is required for inerting the combustible dusts in table 32 that have lower explosion limits (L_{25}) of less than 0.1 g/L in air; the most reactive dusts required about 90 pct. For the combustible dusts with lower limits greater than 0.1 g/L, the inert dust limit was between 25 and 55 pct. The Pittsburgh coal dust from the Bruceton Mine (L_{25} = 0.055 g/L) required 60 pct inert to prevent propagation in these laboratory experiments. The effectiveness of the calcined fuller's earth is comparable to that of a limestone rock dust ($CaCO_3$).

Certain salts of alkali metals and other chemical flame inhibitors are more effective than purely inert materials in preventing or suppressing dust explosions. Table 33 (*31*,

Table 32. — Inerting requirements to prevent propagation of combustible dusts in air-nitrogen, air-carbon dioxide, and air-inert dust (fuller's earth) mixtures at ~25° C (spark ignition)[1]

Combustible	Lower explosion limit (L_{25}), g/L	Minimum oxygen limit, vol pct air-CO_2	Minimum inert dust limit, wt pct
AGRICULTURAL DUSTS			
Cellulose	0.055	13	80
Cornstarch	.045	11	90
Cottonseed meal	.055	15	75
Lycopodium	.025	13	90 +
Soybean meal	.06	15	65
Sucrose	.045	14 (10 in N_2)	85
Wood flour	.035	17	80
CARBONACEOUS DUSTS			
Asphalt, brown petroleum	0.025	NA	90
Charcoal, hardwood	.14	17	55
Gilsonite, Utah	.02	NA	90
Pitch, coal tar	.035	NA	75
Coal, lignite, California	.03	NA	85
Coal, lignite, North Dakota	.045	15	75
Coal, bituminous, Pratt, AL	.12	18	40
Coal, bituminous, No. 7, Illinois	.04	15	75
Coal, bituminous, Whitesburg, KY	.05	NA	60
Coal, bituminous, Bruceton, PA	.055	17	60
CHEMICAL AND PLASTIC DUSTS			
Acetal resin, polyformaldehyde	0.035	11	90 +
Acrylonitrile polymer	.03	13	90 +
Ascorbic acid	NA	15 (12 in N_2)	NA
Cellulose acetate	.04	13 (9 in N_2)	85
Diallyl phthalate	.03	NA (10 in N_2)	NA
Epoxy resin (*no additives*)	.02	12	90
Ethylene-maleic anhydride copolymer	.095	14 (11 in N_2)	70
Ethylene oxide polymer	.03	12	90
Hexamethylenetetramine	.015	14	90 +
Melamine formaldehyde (no plasticizer)	.085	17	55
Methyl methacrylate polymer	.03	11	80
Nylon polyamide	.03	13	90
Paraformaldehyde	.04	12 (8 in N_2)	90
Phenolformaldehyde, 1-step	.025	14	90
Phthalic anhydride	.015	14	90
Polyethylene, high-pressure process	.02	13	90 +
Polystyrene, clear	.02	14	90 +
Polyvinyl acetate	.04	17	75
Rubber, crude, hard	.025	15	90
Urea formaldehyde, spray-dried	.135	16	25

NA Not available.
[1]Based upon data in references 37, 38, 76, and 77.

Table 33. — Incombustible requirements to prevent or suppress propagation of Pittsburgh coal dust with various dust inhibitors in small- and large-scale experiments, weight percent[1]

	$NH_4H_2PO_4$ (ABC powder)	NaCl (salt)	KCl	$NaHCO_3$	$CaCO_3$ (rock dust)	$KHCO_3$ (Purple K)
Hartmann apparatus[2]	NA	50	NA	NA	60	>60
Large gallery[3]	25	30	35	>60	70	>75
Experimental mine[3]	NA	<50	NA	NA	75	>75

[1]Includes inhibitor and ash in coal (6 to 8 pct)
[2]Data from reference 31 with modified apparatus.
[3]Data from reference 88; gallery values taken from graph.

88) compares the effectiveness of six dry powder-type extinguishants against Pittsburgh coal dust explosions in recent small- and large-scale Bureau experiments; note that agent effectiveness was least in the full-scale mine experiments. These data indicate the following ratings for the extinguishants:

$$NH_4H_2PO_4 > NaCl > KCl >> NaHCO_3 > CaCO_3 > KHCO_3.$$

The poor effectiveness of purple K ($KHCO_3$) relative to rock dust ($CaCO_3$) contradicts many earlier data that were obtained under marginal ignition or apparatus-limited conditions; therefore, such data are not reported here. The ABC powder ($NH_4H_2PO_4$ - orthoammonium phosphate) has proved to the most effective dust explosion suppressant. Similar inerting or extinguishing effectiveness of these agents may be assumed applicable to the other combustibles in table 32 that have chemical constituents like those of coal.

Inerting requirements for dust explosions vary with the coal volatility. Figure 69 shows a calculated explosibility diagram by Richmond (*89*) for three coal dusts of different volatility and varying incombustible content; the incombustible included rock dust and ash content (6 to 8 pct) of the coal dusts. The predicted inerting limits from the nose of each curve are 63, 76, and 80 pct for pulverized coals of 17 pct (Pocahontas), 29 pct (Sewell), and 36 pct (Pittsburgh) volatility, respectively. Corresponding limits for such volatile coals in the Bureau's mine experiments were 43, 65, and 73 pct rock dust with a relatively "weak" ignition source; a weak source was defined as a methane-air zone plus coal dust which produces a flame speed of about 50 m/s and flame travel of about 15 m. Calculated values are reported to give best agreement with experimental values obtained with "strong" ignition sources, which are also encountered in mine explosions.

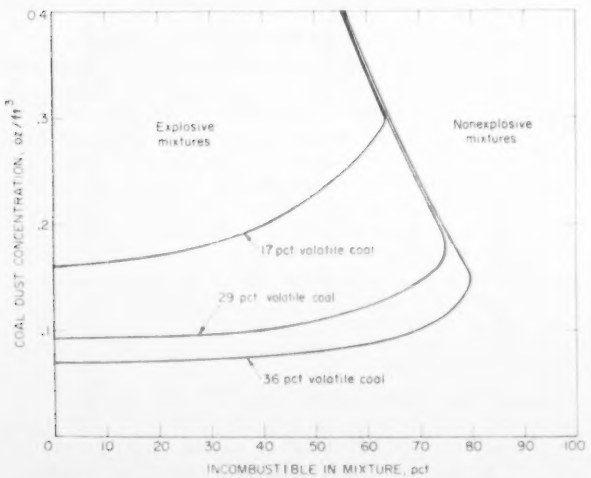


Figure 69.—Calculated limits of explosibility of coal dust-incombustible mixtures for coals of 17, 29, and 36 pct volatility.

IGNITION REQUIREMENTS

Ignition Energies

As with metal dusts, spark ignition energy data for organic dusts are subject to great experimental uncertainties, particularly in the measurement of absolute minimum values. The most complete data for the various classes of combustible dusts are included in the previously cited reports by Nagy, Jacobson, and coworkers. In summary, their data with dust clouds in air indicated that the minimum spark ignition energies of many agricultural, carbonaceous, chemical, and plastic dusts (minus 74 μm) are about 100 mJ or less. Those that required much higher ignition energies included low-volatility carbonaceous materials, fire-resistant chemicals and plastics, and materials with mineral fillers. Coals of high volatility typically had ignition energies of about 50 mJ in air and 10 mJ in oxygen. Coals of low volatility appear to have ignition energies of the order of joules in air and millijoules in oxygen; most such coals did not ignite in air under the spark ignition conditions of the particular study (*76*).

Ignition Temperatures

Bureau data on the minimum ignition temperatures of the various organic dusts in air are also summarized in table 31 (*14, 37-38, 76*). These data were obtained using layered and dispersed dusts (minus 74 μm) in the Godbert-Greenwald apparatus (0.3 L). The dust cloud ignition temperatures are between 400° and 600° C for most of the combustibles investigated; sulfur (190° C), nitrosamine (270° C), and synthetic or crude rubber (320°-350° C) are the few materials that have noticeably lower values. The dust layer ignition temperatures should be noticeably lower than the dust cloud values, although some data are inconsistent. These data are primarily applicable to heating durations of the order of a second for dust clouds and a few minutes for dust layers. Lower ignition temperatures result when the heating duration (residence times) are longer. Table 34 shows the reductions of dust cloud autoignition temperatures that are possible by increasing the volume of the Godbert-Greenwald furnace to 1.2 L and the dust residence time to several seconds. In the case of the dust layer ignition temperatures, these should not be confused with spontaneous heating temperatures that are associated with extended reaction times and adiabatic conditions.

The effectiveness of various dry powder inhibitors on the ignition temperature of Pittsburgh coal dust (minus

Table 34. — Comparison of dust cloud minimum autoignition temperatures in standard and modified Godbert-Greenwald apparatus

	Autoignition temperature, ° C	
	Standard apparatus[1] (0.3 L)	Modified apparatus[2] (1.2 L)
Anthracite coal	840 (4 pct volatile)	780 (6.6 pct volatile)
Bituminous coal (Pocahontas)	640	625
Bituminous coal (Pittsburgh)	610	560
Subbituminous coal (Wyoming)	NA	455
Gilsonite (Utah)	580	490
Lycopodium	480	435
Polyethylene	450	400

NA Not available.
[1]References 37-38, 76.
[2]Reference 10.

74 μm) was determined in the Godbert-Greenwald apparatus by Liebman and Richmond. Their data are shown in figure 70, which was taken from reference 10. These data provide an explanation for the greater effectiveness of NaCl, KCl, and $NH_4H_2PO_4$ as compared to $CaCO_3$, $NaHCO_3$, and $KHCO_3$ in suppressing coal dust explosions; note the agreement between this figure and table 33.

Spontaneous Heating Temperatures

Agricultural and carbonaceous dusts are the most common types of organic materials that may undergo spontaneous heating at normal or slightly elevated temperatures. Spontaneous heating is also referred to as self-heating or spontaneous combustion. It is usually associated with slow oxidation (days) of a combustible under near-adiabatic conditions, as in a large storage bin or pile. Agricultural dusts containing vegetable oils or other highly oxidizable oils are particularly susceptible to self-oxidation. Many coals and charcoals present a similar hazard.

Of the organic combustibles capable of spontaneous heating, coals by far have been the most completely investigated. The most recent and comprehensive study on various U.S. coals was that by Kuchta (*58*), who used a small adiabatic-type apparatus to determine the actual spontaneous heating temperatures. The data showed that dried

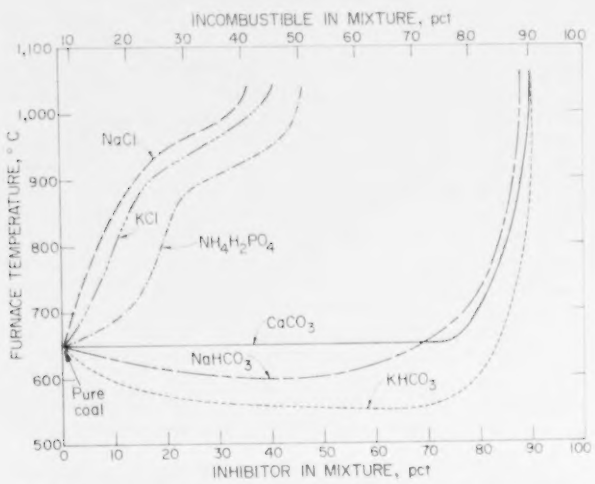


Figure 70.—Effectiveness of various powdered inhibitors on the furnace autoignition temperature of Pittsburgh coal dust in the Godbert-Greenwald furnace.

lignite and subbituminous coals of 100 to 200 mesh could readily self-heat in moist air at 30° C, as compared to 60° to 70° C for western bituminous coals and 80° to 100° C for eastern coals (table 35); heating durations were generally limited to a maximum of about 2 days. Although some western bituminous coals showed a slight tendency to self-heat at 30° C, the exothermic reactions were not sustainable in this apparatus. The heat of wetting (condensation) is believed to be important as a triggering mechanism in these reactions; temperature rises of at least 10° C were reported in experiments with a dried coal and moist nitrogen. Sondreal (*97*) found that the calorific heats of wetting can be as high as 26, 20, 7 and 1 cal/g for dried lignite, subbituminous, Illinois bituminous, and Pittsburgh bituminous coals, respectively. Thus, the weathering of coals increases their spontaneous combustion hazard.

Table 35. — Spontaneous heating temperatures and CO-ΔO_2 indexes of various dried coal dusts in air (*58*)

Coal	Spontaneous heating[1] temperature, ° C	CO/ΔO_2[2], ppm/vol pct
LIGNITE		
Beluga, Alaska	32	198
Gascoyne strip, North Dakota	30	244
Husky strip, North Dakota	30	246
Sandow strip, Texas	30	228
SUBBITUMINOUS		
Dravo, seam No. 80, Wyoming	30	285
Jim Bridger, Wyoming	32	188
Sarpy Creek, Rosebud, Montana	30	178
Sarpy Creek, Stray No. 2, Montana	30	216
BITUMINOUS		
Pittsburgh, Pennsylvania	80	74
Pocahontas No. 3, West Virginia	90	66
Powhatan, No. 3, Ohio	105	49
Sahara, No. 20, Illinois	60	75
Scotia, Kentucky	70	48
Somerset No. 1, Colorado	60	119
Sunnyhill No. 9, Ohio	70	110
Sunnyside No. 1, Utah	70	178

[1]100- to 200-mesh coals.
[2]10- to 20-mesh coals.

The tendency of coals to self-heat may be roughly predicted from their CO-ΔO_2 index, which is a measure of the coal's ability to adsorb oxygen from the atmosphere and form or evolve carbon monoxide. Closed vessel desorption experiments (*58*) showed that the CO-ΔO_2 index is greatest for dried crushed coals and becomes near-maximum after several days' exposure in air (fig. 71). Table 35 includes the CO-ΔO_2 index values that were obtained in such experiments after 7 days with 10- to 20-mesh samples of the coals in air at 25° C; here, the CO formation or desorption is in parts per million, and oxygen reduction (ΔO_2) is in volume percent. Essentially, the most reactive coals have a CO-ΔO_2 index close to 200 or more, and the least reactive ones less than about 100. Proximate and ultimate analyses of the coals are included in table 36. The CO-ΔO_2 ratios correlate best with the oxygen content of the coals. They are strongly dependent upon temperature and about an order of magnitude less than corresponding CO-CO_2 ratios (fig. 72) (*58*). Such data can be useful in predicting the temperature of the given coals during their incipient combustion before autoignition. In a mining environment, the CO-ΔO_2 index is often found to be at least 1/2 lower than the laboratory closed-vessel value; this is attributable to experimental artifact or complex dilution effects in mine ventilation networks.

Table 36. — Analyses of coals as received

Mine	Location	Heating value, Btu/lb	Proximate analysis, wt pct				Ultimate analysis, wt pct					
			Moisture	Volatile matter	Fixed carbon	Ash	Hydrogen	Carbon	Nitrogen	Oxygen	MAF[1] oxygen	Sulfur
LIGNITE												
Beluga	Alaska	7,000	24.5	31.1	28.9	15.5	5.9	42.0	0.7	35.8	23.3	0.1
Gascoyne strip	North Dakota	7,150	34.0	29.5	30.2	6.3	6.7	43.0	.8	41.9	19.6	1.3
Husky strip	North Dakota	7,280	34.1	30.7	29.0	6.2	7.0	42.7	.6	42.8	20.9	.6
Monticello	Texas	7,430	29.4	31.9	27.7	11.0	6.4	43.3	1.2	37.6	19.2	.6
Center strip	North Dakota	7,660	32.0	32.5	30.9	4.6	6.7	46.1	.7	41.5	20.6	.4
Darco strip	Texas	7,850	31.1	30.5	32.5	5.9	6.6	46.1	.8	39.7	19.1	1.0
Sandow strip	Texas	8,940	21.1	39.5	29.1	10.3	6.4	50.8	.9	30.6	17.3	1.0
SUBBITUMINOUS												
Sarpy Creek, Rosebud	Montana	9,330	22.0	32.5	39.4	6.1	6.2	54.6	0.7	31.9	17.2	0.5
Sarpy Creek, Stray No. 2	Montana	9,460	18.5	33.5	37.8	10.2	5.9	54.5	.7	27.9	16.1	.8
Dravo, seam No. 82	Wyoming	10,620	14.7	33.0	47.7	4.6	5.8	61.7	1.4	25.6	15.7	.9
Jim Bridger	Wyoming	10,740	15.7	31.6	49.9	2.8	5.8	62.6	1.0	27.4	16.4	.4
P&M, Mammoth	Montana	11,130	11.2	38.2	46.9	3.7	5.4	65.9	1.1	23.5	16.0	.4
Dravo, seam No. 80	Wyoming	11,190	11.7	38.0	46.9	3.4	6.0	64.1	1.7	24.2	16.2	.6
BITUMINOUS												
Sunnyhill No. 9	Ohio	11,520	8.2	35.9	46.3	9.6	5.4	65.5	1.3	15.7	10.2	2.5
Inland No. 6	Illinois	12,370	6.2	30.5	55.4	7.9	5.2	70.8	1.6	14.0	9.8	.5
Prince	Nova Scotia	12,580	3.2	35.1	52.4	9.3	4.9	69.7	1.3	10.1	8.2	4.7
Sahara No. 21	Illinois	12,650	4.5	32.7	54.2	8.6	5.2	71.1	1.5	11.2	8.2	2.4
Sahara No. 20	Illinois	12,760	6.5	33.8	52.4	7.3	5.2	71.5	1.6	12.3	7.5	2.1
Napoleon	Ohio	12,830	6.2	43.3	45.1	5.0	5.7	70.6	1.4	14.2	9.8	3.1
Sunnyside No. 1	Utah	13,060	4.7	37.4	53.2	4.7	5.5	73.5	1.5	13.6	10.3	1.2
Somerset No. 2	Colorado	13,250	2.7	37.6	53.7	6.0	5.4	74.4	1.5	12.2	10.7	.5
Somerset No. 1	Colorado	13,770	3.8	39.1	54.2	2.9	5.8	76.5	1.6	12.6	9.9	.6
York Canyon	New Mexico	13,680	1.4	35.9	53.9	8.8	5.3	75.7	1.6	8.2	7.6	.4
Allison	Ohio	13,660	2.5	43.5	46.3	7.7	5.4	73.2	1.3	7.1	5.6	5.3
Powhatan No. 3	Ohio	13,690	2.9	41.5	50.7	4.9	5.6	76.3	1.7	9.2	7.1	2.3
Vail	Ohio	13,780	4.1	41.2	50.3	4.4	5.6	75.6	1.6	10.2	7.3	2.6
Scotia	Kentucky	13,850	1.6	35.1	54.1	9.2	5.1	76.0	1.2	7.9	7.3	.6
Bruceton	Pennsylvania	14,500	1.5	38.9	55.8	3.8	5.6	79.7	1.8	7.9	6.9	1.2
Pocahontas No. 3	West Virginia	14,360	2.7	16.3	75.9	5.1	4.5	84.1	1.1	4.6	2.6	.6

[1]Moisture and ash free.

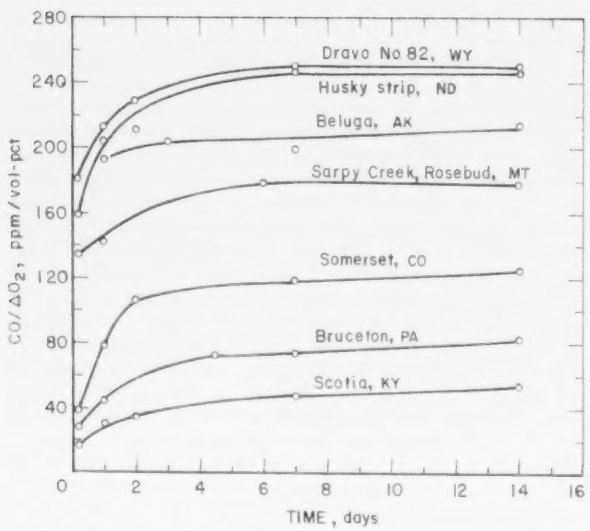


Figure 71.—CO-ΔO_2 ratio versus time in closed-vessel desorption experiments with seven coals of 10 to 20 mesh in air at 25° C.

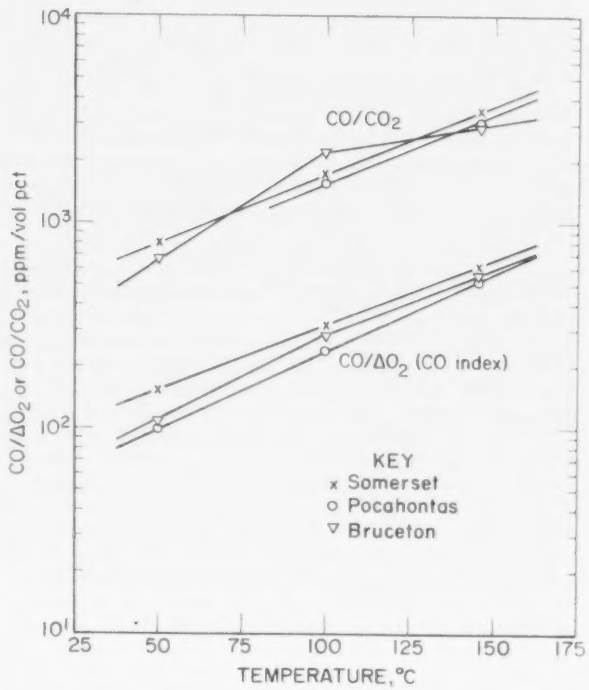


Figure 72.—Variation of CO-ΔO_2 and CO-CO_2 ratios with temperature in a flowing airstream (15 cm_3/min) with three undried coals of 10 to 20 mesh.

The total gas content of a coal can be useful in predicting both spontaneous heating and explosion hazards, even though methane or other gases in the coal are not known to be vital to the spontaneous combustion process. Figure 73 illustrates this point with ASTM designations for coal rankings. The gas content data are average values of gas desorption measurements by Diamond (*12*) for virgin core samples from 125 coalbeds; they represent total gas desorptions of cored and crushed samples for periods up to 1 month or when the degasification rates become very low. Of practical significance is that the self-heating hazard increases whereas the gas explosion hazard decreases with decreasing gas content or rank of the coal; the coals in table 36 are listed in the order of increasing calorific value, which also indicates their approximate ASTM coal ranking. Although all coals are capable of self-heating at some threshold temperature, the incidence rate is small for those with a gas content of about 4 cm^3/g or greater; this corresponds to a high-volatile A bituminous or higher rank coal. In evaluating the gas explosion potential of any coal, one can assume that most of its gases will be released during the mining stage; also, the residual gases will be released at a slower rate for the higher rank coal.

Other organic dusts that are widely known to undergo self-heating at normal ambient temperature are those containing linseed, cottonseed, rapeseed, or olive-type vegetable oils. Cereal grains, hay, and even grass clippings have this capability during their curing or storage. Most other organic solids require elevated temperatures to self-heat and present a potential ignition hazard. Table 37 lists the spontaneous heating temperatures that were obtained by the National Bureau of Standards (*72*) for various woods, fibrous materials, and synthetic rubbers. The data for rubber materials indicate the great effect of particle size or physical form of the combustible solid.

Table 37. — Spontaneous heating temperatures of various woods, fibrous materials, and synthetic rubbers in air

Material	Sample type	Spontaneous heating temperature, °C
WOODS AND FIBROUS MATERIALS		
Douglas fir	Shavings	260
Spruce	Shavings	261
Long leaf pine	Shavings	230
Short leaf pine	Shavings	228
White pine	Shavings	264
Paper, filter	Cuts	232
Paper, newsprint	Cuts	230
Cotton, absorbent	Roll	266
Cotton, batting	Roll	230
Cotton, sheeting	Roll	240
Nylon, parachute	Roll	475
Silk, parachute	Roll	570
Viscose rayon, parachute	Roll	280
Wool, blanket	Roll	205
Cane fiberboard	Piece	240
Wood fiberboard	Piece	220
SYNTHETIC RUBBERS		
GR-S, black	Buffings	160
GR-S, black	Coagulum	295
GR-S (R-60), black	Buffings	190
GR-S (R-60), black	Coagulum	310
GR-S, indulin	Crumb	440

[1]Data from reference 72, 13th ed., 1969, sec. 5, p. 213.

Sulfide ores, such as iron sulfide, are well known to oxidize spontaneously in moist air. Temperatures in such reactions can be sufficient to ignite timbers, coals, and other organic material.

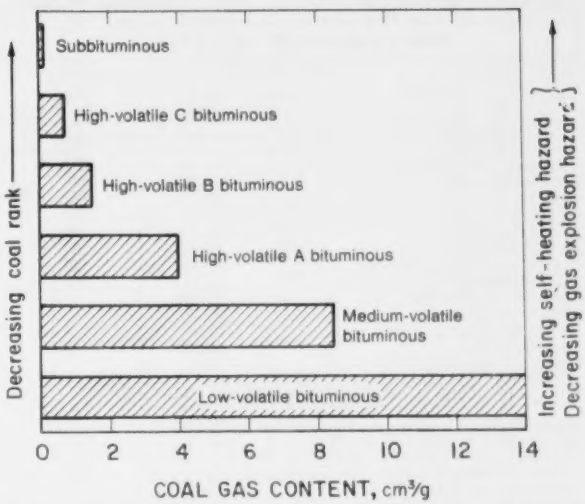


Figure 73.—Representative gas contents of various ranked coals and their relative hazard potential for self-heating and gaseous explosion.

FLAME TEMPERATURES AND BURNING RATES

Flame Temperatures

The flame temperatures of most organic dusts have not been determined, and those that have been are not as precisely defined as for organic liquid vapors or gases. Nevertheless, their flame temperatures should be comparable to those of the hydrocarbons or other classes of chemical constituents that are present. For example, Hertzberg (*31*) obtained a maximum flame temperature of approximately 2,100° C in explosions of Pittsburgh coal dust-air mixtures, which is comparable to the *constant-volume* combustion values calculated for many stoichiometric hydrocarbon vapor-air mixtures. The maximum value of 2,100° C was found at a coal dust concentration of 300 mg/L, and a near-lower-limit value of 1,300° to 1,400° C was obtained at a dust concentration of 150 mg/L. Corresponding flame temperatures for other carbonaceous or organic dusts should roughly fall in this temperature range if their chemical constituents are largely hydrocarbons or hydrocarbon derivatives similar to those found in coals. For any composite dust, the flame temperature will decrease with increasing amounts of incombustible material.

Burning Rates

Compared to hydrocarbon vapor-air mixtures, the fundamental burning velocities (S_u) of organic dust-air mixtures appear to be noticeably lower, although only meager data are available. For Pittsburgh coal dust-air mixtures, the calculated S_u values from measured flame speeds ranged from 4 to 18 cm/s for dust concentrations of 150 to 500 mg/L (*31*). The maximum S_u of 18 cm/s is at least 1/2 lower than those reported for gaseous hydrocarbons (table 17).

In the case of fires with combustible solids, their burning rates or flame spread rates are useful in determining how rapidly the fires may propagate. Table 38 gives horizontal burning rates that were obtained by Bureau investigators for small beds of various flammable granular

Table 38. — Burning rates (horizontal) of flammable granular solids and oxidizer-sawdust mixtures in air at 1 atm (decreasing order of flammability)

Material	Particle size, mesh	Burning rate, cm/min
FLAMMABLE SOLIDS (1.25- BY 1.25- BY 12.5-CM BED) (*60*)		
Phosphorus sesquisulfide	50-150	[1]290
Phosphorus, red	100-200	225
Titanium	100-200	190
Camphor	10-30	89
Magnesium	>80	[1]76
Sodium methylate	70-150	74
Picric acid, 10 to 20 pct H_2O	10-50	19
2,4-Dinitroaniline	40-70	16.5
Ammonium dichromate	30-100	10.2
Phthalic anhydride	20-70	[1]9.7
Sodium borohydride	10-30	8.6
Tetraphenyl tin	50-200	6.9
Charcoal, willow wood	40-50	[1].8
OXIDIZERS + SAWDUST (2.5- BY 5- BY 18-CM BED) (*55*)		
Sodium peroxide (70 pct)	40-150	2,160
Calcium hypochlorite-69.5 pct Cl_2 (80 pct)	20-100	305
Potassium bromate (60 pct)	70-100	290
Chromium trioxide (80 pct)	20-100	230
Ammonium perchlorate (80 pct)	20-100	105
Sodium perchlorate (70 pct)	20-100	76
Potassium nitrate (40 pct)	40-100	71
Sodium nitrate (40 pct)	40-150	61
Sodium chlorate (60 pct)	20-70	48
Potassium permanganate (60 pct)	20-100	30
Lead nitrate (50 pct)	50-150	12
Potassium persulfate (80 pct)	30-150	10
Potassium dichromate (70 pct)	30-100	8.9
REFERENCE SAWDUST (2.5- BY 5- BY 18-CM BED)		
Red oak, select grade (dried)	20-50	6.9

[1]0.65- by 1.25- by 12.5-cm bed.

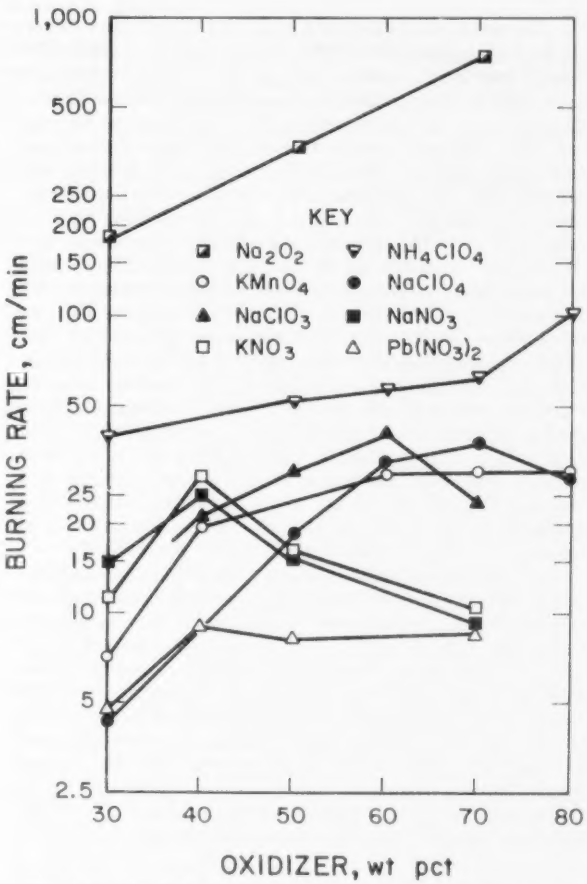


Figure 74.—Variation of burning rate with oxidizer concentration for dried sawdust (red oak) with various solid oxidizers.

solids (*60*); these data actually represent flame spread measurements over the burning surface. Although particle size was not held constant, the data provide a good indication of the flame spread potential of each material, including such hazardous metal dusts as magnesium and titanium. Higher burning rates are normally expected with finer dusts, provided particle agglomeration does not occur. Materials having a burning rate less than 10 cm/min are considered to present a low flame spread hazard. With the exception of sodium borohydride, the flame spread ratings found by these authors were consistent with ignitability ratings by a flame source.

Table 38 also includes burning rates for mixtures of dried sawdust of a select grade red oak with a number of oxidizers (*55*). The rates are maximum values obtained at optimum oxidizer concentrations; oxidizer concentration effect is shown in figure 74. These data are indicative of the increased fire hazard that may result when a cellulosic packaging material, such as wood, is involved in fires with oxidizer cargoes. Note that the burning rate of the sawdust (~7 cm/min) is substantially increased with the addition of most oxidizers, including the alkali metal nitrates, chlorates, and perchlorates. The highest rate (2,160 cm/min) by far was obtained with the very strong oxidizer of sodium peroxide. In any application of these data, one must allow for the increased flame spread that can result from scaling and ventilation effects.

PROPERTIES OF FABRICS AND SHEET COMBUSTIBLES

IGNITION TEMPERATURES

Combustibles in sheet form can require relatively high temperatures for their ignition. Bureau data (*56*) for 10 representative fabric- or sheet-type combustibles are given in table 39. Such common materials as paper drapes and cotton or rubber sheeting require about 400° C for ignition in air when uniformly heated (vessel ignitions); other sheet combustibles such as wool, cellulose acetate, polyvinyl chloride, and Nomex require over 500° C for ignition; Nomex is a fire-resistant nylon. When the heating is nonuniform, as with a hotplate, the ignition temperatures are substantially higher than the vessel ignition temperatures; also, they are lower in oxygen than in air, as one would predict. Although fire-retardant additives usually increase the ignition temperature, some may actually increase the ignition hazard; note data for the treated cotton sheeting that contained an ammonium salt fire retardant. In addition, the values in oxygen (1 atm) were found comparable to or less than those in air at 6 atm, indicating the dependence on oxygen partial pressure.

Table 39. — Ignition temperatures of flammable fabric or sheet materials in air and oxygen at atmospheric pressure (*56*)

Material	Density, g/m²	Ignition temperature, °C		
		Heated vessel	Hotplate	
		with air	Air	Oxygen
Cellulose acetate sheet	363	550	>600	425
Conductive rubber sheeting	500	390	480	360
Conductive Tygon tubing	NA	415	NA	NA
Cotton sheeting	160	385	465	360
Cotton sheeting, fire retardant	NA	430	575	310
Nomex sheeting	102	515	>600	520
Paper drapes	53	400	470	410
Plexiglass sheet	807	450	595	430
Polyvinyl chloride sheet	495	560	>600	390
Wool blanket	712	540	>600	500

NA Not available.

BURNING RATES

Flame spread rates of sheet combustibles provide a measure of their surface burning rates. Such data are given in table 40 from the above-cited work (*56*) where the upward flame propagations were determined with small samples (5- by 25-cm) at a 45° angle in air and oxygen at atmospheric pressure. Under these conditions, many of the combustibles failed to sustain propagation in air. Even in oxygen, only the paper drapes (19.6 cm/s) and wool blanket (100 cm/s) gave relatively high rates; the high value for wool is attributable to "nap" burning. The rates in oxygen atmospheres correlate well with total pressure or oxygen partial pressures (fig. 75); the pressure dependence was greatest for cotton sheeting (rate α $P^{0.95}$) and least for rubber sheeting (rate α $P^{0.55}$). In comparison, the rates in various oxygen-nitrogen atmospheres were not as sensitive to oxygen partial pressure.

Flame spread rates are always greater when the combustibles are burned in a vertical orientation in the upward mode. For example, upward verticle rates for cotton sheeting in air were 20 times greater than horizontal rates and 40 times greater than vertical downward rates. The rates can also be greatly influenced by the combustible loading, combustible distribution, air ventilation rate, and other fire enhancement factors. Hence, the laboratory-scale data cannot be assumed to provide a measure of the maximum fire hazard that may be encountered in a large-scale fire situation.

The fire resistance characteristics of several mine conveyor belts are given in table 41. These data were obtained by the Bureau (*59*) in a moderately scaled apparatus (48 by 48 by 168 cm) with a flame ignitor input of 50 kcal/min (~1.6 cal/(cm²·s)) and air velocity of 30 m/min. Horizontal flame spread rates under such conditions ranged from 0 to 12 cm/min depending upon the type of belt, as compared to 21 cm/min for a red oak standard. To define the overall fire resistance rating for each belt, a flammability index (FI) is given that includes the contributions of the flame spread rate (FS), heat release rate (Q_f), and critical ignitor input (I, time-integrated heat flux); this index ($FI = FS \times Q_f/I$) is also normalized with respect to red oak. The fire resistance ratings by this method were found to be more reliable than those obtained by small laboratory-scale methods. The use of air velocities greater than 30 m/min can give higher flame spread rates, although ignitions become increasingly difficult to achieve. Also, a belt height-chamber height ratio of about 0.75 appears optimum for sustained propagation in a tunnel-type fire. Both ignition and flame propagation stages must be considered in determining belt fire resistance.

Table 40. — Flame spread rates (45° angle) of flammable fabric or sheet materials in air and oxygen at atmospheric pressure (*56*)

Material	Density, g/m²	Flame spread rate, cm/s	
		Air	Oxygen
Cellulose acetate sheet	363	NP	2.8
Conductive rubber sheeting	500	NP	3.3
Cotton sheeting	160	2.0	8.1
Cotton sheeting, fire-retardant	NA	NP	4.3
Nomex sheeting	102	NP	4.3
Paper drapes	53	5.1	19.6
Plexiglass sheet	807	.5	1.3 (42 pct O_2)
Polyvinyl chloride sheet	495	NP	2.5
Wool blanket	712	NP	100
Wood strips, white pine	1,670	.5	2.8

NA Not available. NP No sustained propagation.

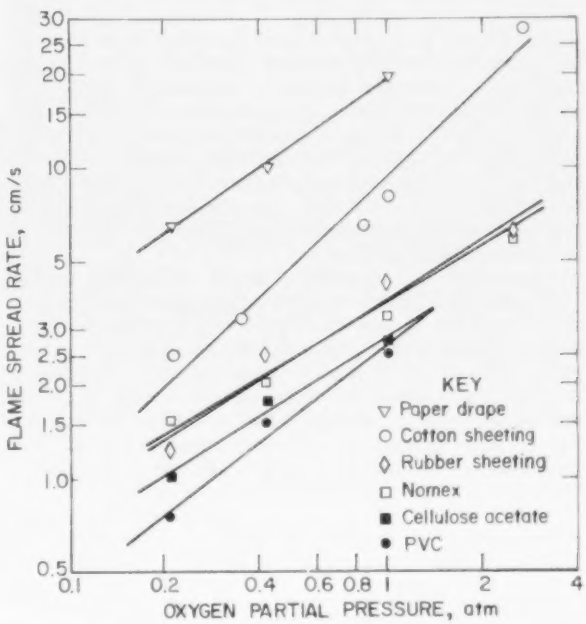


Figure 75.—Effect of oxygen pressure on the flame spread rates of sheet combustibles in oxygen atmospheres.

Table 41. — Flammability data for mine conveyor belts and red oak standard in Bureau of Mines belt flammability apparatus (*59*)[1]

Combustible	Flame spread rate (FS), cm/min	Heat release rate (Q_t), cal/(cm²-min)	Critical ignitor input (I), cal/cm²	Flammability index[2] (FI)	Normalized flammability index (FI')
REFERENCE STANDARD MATERIAL					
Red oak	20.8	230	145	33	100
CONVEYOR BELTS					
Non-fire-resistant rubber (Goodyear)	10.9	213	145	16	48
Neoprene (Goodyear-A)	10.6	165	240	7.3	22
Polyvinyl chloride (Fenner America)	12.2	122	335	4.4	13
Fire-resistant rubber (Goodyear)	5.8	60	335	1.0	3.0
Neoprene (Goodyear-B)	7.2	76	820	.7	2.1
Polyvinyl chloride (Scandura)	7.3	75	1,295	.4	1.2
Polyvinyl chloride (Georgia Duck)	NI	NI	>1,440	0	0
Polyvinyl chloride[3] (German Clouth)	0-4.6	0-71	>865	0-.4	0-1.2
Neoprene (German Clouth)	NI	NI	>2,400	0	0

NI No ignition at given ignitor input.
[1]Ignitor input — 50 kcal/min (1.6 cal/(cm²-s)). Air velocity — 30 m/min.
[2]$FI = \frac{FS \times Q_t}{I}$.
[3]Only 1 ignition in 4 trials.

FIRE AND EXPLOSION DAMAGE

FIRE TEMPERATURE AND RADIATION CRITERIA

Fire damage to materials results primarily from exposure to the high levels of temperature and thermal radiation produced by the fire. Qualitative guidelines for analyzing fire damage are summarized in the section on investigative procedures. Supporting data for such analyses are found in this section and in the other sections that characterize the fire properties of various materials. Considering that maximum flame temperatures of many combustible-oxidant systems can be 2,000° C or more, as in table 17, constructional and appurtenant materials cannot withstand a large-scale fire for long durations without being consumed or severely damaged. Fortunately, most fires involve diffusional flames, which are less severe than premixed flames. The extent of any fire damage will be largely determined by the fire loading on the exposed material and its meltability, combustibility, and massiveness or fineness. Fire loading itself is the temperature and heat flux generated by the fire under the particular static or dynamic environmental conditions.

Some useful temperature limits of various textile fibers and metallic or nonmetallic composite materials are given in tables 42 and 43, respectively. Melting points of pure elements and compounds are included in the summary tables of this manual for each class of combustibles; the ignition temperature data are also useful in determining temperature limitations of materials. Among the highest melting point substances are graphite (3,700° C), molybdenum (2,617° C), tantalum (2,996° C), tungsten (3,410° C), and the refractory compounds. Steel is one of the most common materials of construction and has a melting point of about 1,400° C or more. The brightness or color of such metals in a fire can be used to estimate their temperatures (table 44).

Damage may occur even in the absence of flaming combustion, as in the self-heating of coals, which may result in a loss of their calorific values. Generally, if the temperature rise from self-heating is small (~10° C), any calorific loss of the coal that does occur will be very small. However, if the temperature rise is about 30° or more, the calorific loss can be noticeable, depending upon the heating duration and maximum resultant temperature. Proximate and ultimate coal analyses on a moisture-free basis are most useful in determining the self-heating effect on calorific values.

Thermal radiation from a fire can cause property damage and human injury if the incident radiant flux is of sufficient intensity. Data by Lawson (*64*) define the threshold radiation intensities required for igniting various combustible solids and for sensing pain by a human body (table 45). These data are for relatively moderate exposure times and, therefore, do not necessarily represent the lowest values possible for extended exposure periods. For example, the value for ignition of wood (0.8 cal/(cm²-s)) is higher than the usually accepted value of approximately 0.5 cal/(cm²-s) for exposure times of many minutes. The value of 0.1 cal/(cm²-s) for sensing pain can also be considered as an approximate threshold for second-degree burns at exposure times of minutes.

Table 42. — Temperature limits of various textiles (*4*)[1]

Fiber	Temp, °C	Effect	Fiber	Temp, °C	Effect
Acetate	260	Melts.	Polyester	250	Melts.
Asbestos	810	NS.	Polyethylene	110-120	Melts.
Cotton	150	Decomposes.	Polypropylene	160-170	Melts.
Flax	135	NS.	Silk	150	Decomposes.
Glass	730	Softens.	Viscose rayon	175-205	Decomposes.
Jute	135	NS.	Wool	135	Decomposes.
Nylon	215-260	Melts.			

NS Not specifically defined.
[1]Rounded values.

Table 43. — Melting points of metallic and nonmetallic substances[1]

Substance	Melting point, °C
METAL	
Aluminum alloy 38	565
Aluminum alloy 3003	650
Aluminum bronze, ASTM B36	1,040
Bismuth solder	95-130
Carbon steel, SAE 1020	1,515
Cast iron, gray, ASTM A48	1,175
Cast iron, ductile, ASTM A339	1,150
Brass, red, ASTM B30	995
Brass, yellow, ASTM B36	930
Cupronickel, constantan	1,260
Hastelloy C	1,290
Inconel X, annealed	1,400
Magnesium alloy, AZ 3113	625
Monel K	1,330
Nickel-silver alloy, 18 pct	1,110
Stainless steel, type 304	1,425
Tin solder	135-175
Titanium, commercial	1,815
NONMETAL	
Borax	560
Glass, borosilicate	[2]820
Graphite	3,700
India rubber	125
Paraffin	55
Porcelain	1,550
Quartz, clear	[2]1,660
Spermaceti (wax)	50
Stearine (wax)	50

[1]Based upon data in references 4, 83, 105; rounded values.
[2]Softening point.

Table 44. — Color temperatures of iron or steel (*4*)[1]

Metal color	Temp, °C
Dark blood red, black red	530
Dark red, blood red	565
Dark cherry red	635
Medium cherry red	675
Cherry, full red	745
Light cherry, light red	845
Orange	900
Light orange	940
Yellow	995
Light yellow	1,080
White	1,205

[1]Rounded values.

Table 45. — Threshold radiation intensities for various thermal effects (*64*)

Effect	Threshold radiation intensity	
	cal/(s·cm²)	Btu/(h·ft²)
Wood ignites spontaneously	0.8	10,600
Hemp, jute, and flax ignite spontaneously	1.0	13,300
Textiles ignite spontaneously	.85	11,300
Fiberboard ignites spontaneously	.75	10,000
Wood ignites by flying brands	1	1,300
Painted wood ignites by flying brands	4	5,300
Humans feel pain after a short time	1	1,300

The fire radiation received by an object is a function of its distance from the fire source and the size and intensity of the radiant energy source. Yumoto (*109*) defined the irradiance (I) of hydrocarbon-type fuel fires (gasolines) as a dimensionless function of the irradiance distance and diameter of the burning fuel tank. These data are replotted in figure 76 and extrapolated to an ignition threshold for wood (0.45 cal/ (cm²·s)) and to the radiant intensity at a dimensionless ratio (d_o/r_o) of 1 (~5 cal/(cm²·s)), which theoretically corresponds to the source intensity; d_o is the irradiance distance and r_o is the radius of the fuel tank. The negative slope of 2 indicated by these data is consistent with the inverse square dependence with distance that is predicted by equation 33. Thus, if the ignition radiant thresholds are known for hydrocarbon- or carbonaceous-type combustibles as in table 45, figure 76 can be applied to obtain a rough estimate of the distance from a gasoline pool fire source at which ignition could occur. Similar estimates for other liquid fuels can be made using equation 33 and the data in table 21. The variations of irradiances with windy conditions, nonuniform flame symmetry, and different flame emissivities are important in any rigorous treatment.

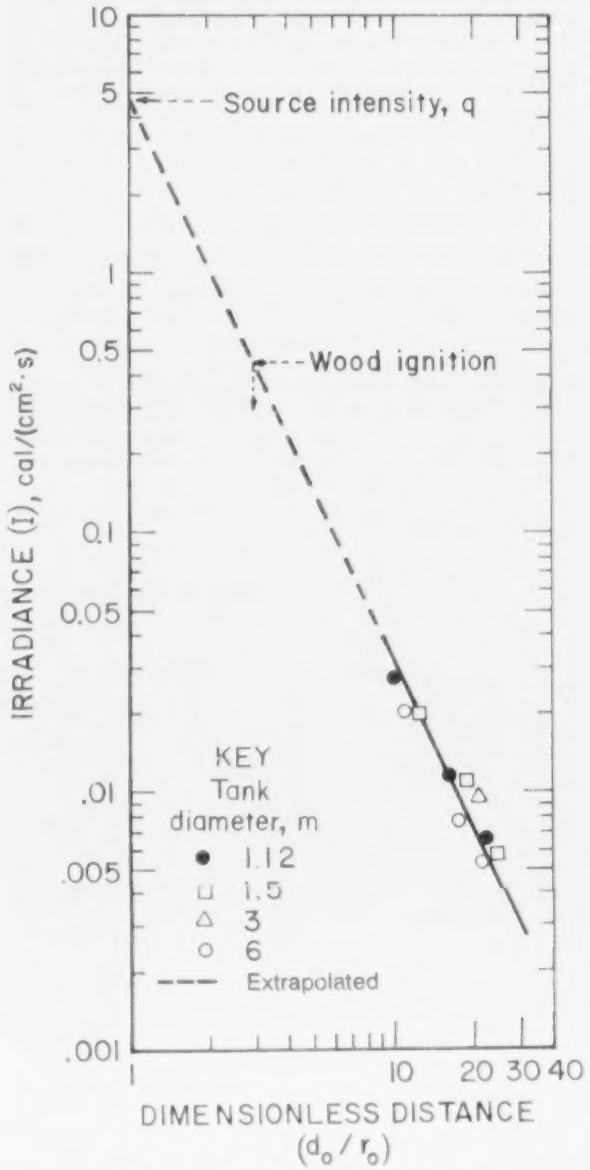


Figure 76.—Thermal irradiance of gasoline tank fires as a function of a dimensionless distance ratio (irradiance distance-tank fire radius).

EXPLOSION PRESSURE CRITERIA

Pressure damage from combustible gas explosions (deflagrations) will depend upon the explosion pressure of the combustible mixture, strength of the confinement material (including fasteners), and degree of any venting. Expressions for calculating explosion temperatures and pressures are given in the section on theory and definitions. Although maximum pressures occur with near-stoichiometric combustible concentrations for complete combustion, even near-limit concentrations yield explosion pressures that may exceed the pressure limits of the confinement material. The methane-air data in figure 77 (*47*) are typical of the fuel concentration effect on explosion pressure for many hydrocarbon combustibles. They are characterized by a maximum pressure rise ratio (P_2/P_1) of about 8 at near-stoichiometric concentrations, as predicted by theory; some calculated adiabatic values are given in table 18.

Failure of a cylindrical or spherical container in such explosions may be estimated from the equations for the two possible types of stress failure:

$$\text{Hoop stress (tangential)} \qquad S_h = Pr/t \qquad (79)$$

$$\text{Tensile stress (longitudinal)} \qquad S_t = Pr/2t \qquad (80)$$

where S is stress (psi), P is pressure (psi), r is container radius (in), and t is container thickness (in); efficiency of any welds is neglected in the above equations but is usually near unity. The most severe explosions will involve hoop stress failure with minimum "thinning down" of the container in areas adjacent to the failure. Table 46 gives the yield and tensile strengths of various metals and alloys that define the maximum stresses for deformation and failure of the materials, respectively. These values are for uniform static loadings; for dynamic loadings, they are at least twice as large.

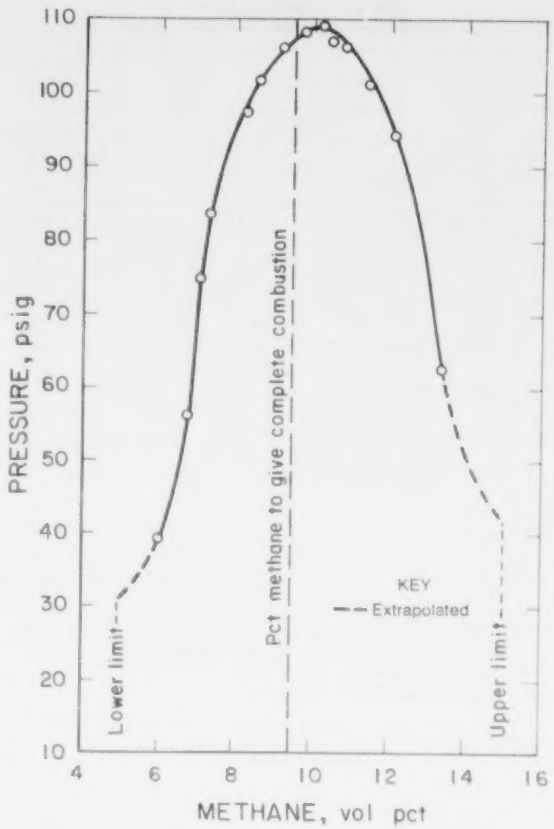


Figure 77.—Effect of fuel concentration on explosion pressures of methane-air mixtures at 25° C and 1 atm.

Table 46. — Mechanical properties of metals and alloys (*83*)

Material	Condition	Yield strength, kpsi	Tensile strength, kpsi
Aluminum alloy (1100)	Annealed	5	13
Aluminum alloy (1100)	Cold-rolled-H 18	22	24
Aluminum alloy (5052)	Annealed	13	28
Aluminum alloy (5052)	Cold-rolled stabilized-H 38	37	42
Aluminum alloy (380)	Die-cast	26	43
Aluminum bronze (612)	Hard	65	105
Brass, red (230)	Cold-rolled	60	75
Copper (102)	Cold-drawn	40	45
Cupronickel (55-45)	Cold-drawn	50	65
Duranickel	Annealed	45	100
Hastelloy (B)	Rolled	56	120
Hastelloy (G)	Sheet	46	102
Incoloy (800)	Annealed	40	90
Inconel (600)	Cold-drawn	100	130
Inconel (610)	As-cast	38	80
Iron, wrought	Hot-rolled	30	48
Iron, gray cast	As-cast	NA	≈25
Magnesium alloy (AZ80A)	Extruded	36	49
Monel (400)	Cold-drawn	80	110
Nickel alloy (220)	Annealed	20	70
Permanickel	Annealed, age-hardened	125	175
Stainless steel (201)	Annealed, strip	50	115
Stainless steel (304)	Annealed	30	85
Stainless steel (304)	Cold-rolled	≈160	≈185
Stainless steel (321 and 347)	Cold-rolled	≈120	≈150
Stainless steel (420)	Heat-treated	200	250
Stainless steel (cast 12 Cr)	Tempered at 315° C	150	200
Stainless steel (cast 20 Cr)	Annealed	60	95
Steel, carbon (SAE 1020)	Hot-rolled	42	68
Tantalum (10W)	Annealed	158	160
Tin	As-cast	NA	2
Titanium (pure)	Annealed	75	85
Zircalloy (2)	Annealed	50	75

NA Not available.

In the case of containments equipped with bolt or screw fasteners, their failure will be determined by the uniform or nonuniform distribution of the pressure loading on all the bolts; the root thread area is used in calculating the loading on a threaded fastener. One should not neglect the stress due to tightening a bolt since this initial load can exceed the tensile strength of ordinary carbon steel material (~60,000 psi) in bolts of less than about 1.25 cm (1/2 in) diameter.

The time at which a vessel or confining structure will fail owing to a gaseous explosion can vary greatly with the combustible-oxidant-diluent mixture and container volume. Figures 78, 79, and 80 (*39*) show the explosion pressure growth rates obtained by Bureau investigators (Johnson, Furno, and Kuchta) in a 3.65-m (12-ft) diameter sphere. In this size vessel, the time to achieve maximum pressure was less than 1 s for the optimum CH_4-air mixture, compared with about 20, 12, and 6 s for near-limit compositions of CH_4-air, CH_4-air-N_2, and CH_4-air-CF_3Br, respectively; note that the effectiveness of the CF_3Br inhibitor tends to be minimal when the pressure rises are above about 30 psig. For ideal spherical explosions at constant flame speeds, the maximum pressure rise rates (dP/dt) or times (t) to maximum pressure may be approximately extrapolated to larger vessel volumes (V) as follows:

$$\frac{(dP/dt)_1}{(dP/dt)_2} = \frac{t_2}{t_1} = \left(\frac{V_2}{V_1}\right)^{1/3} \qquad (81)$$

where the subscripts 1 and 2 refer to the small and large size vessels, respectively. However, this cubic dependence on volume becomes unreliable with the less optimum mixtures or nonspherical propagations, as discussed earlier in connection with equation 49.

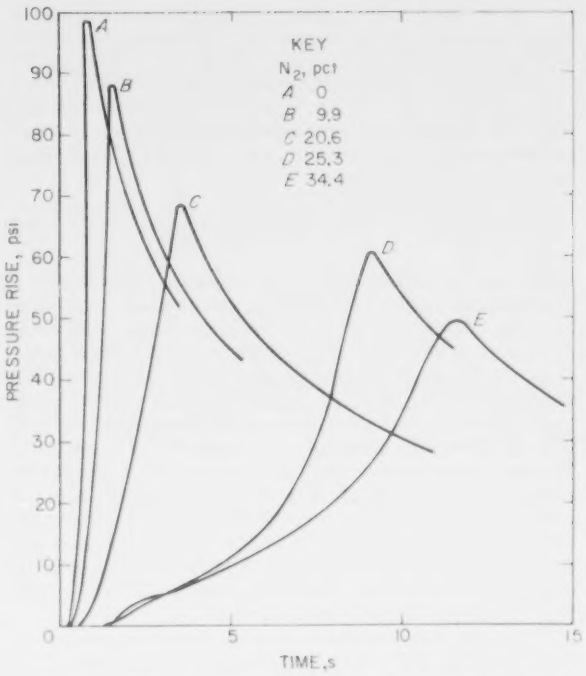


Figure 79.—Explosion pressure growth for 9.5 pct methane-air mixtures and added nitrogen in 3.65-m (12-ft) diam sphere at 25 C and 1 atm.

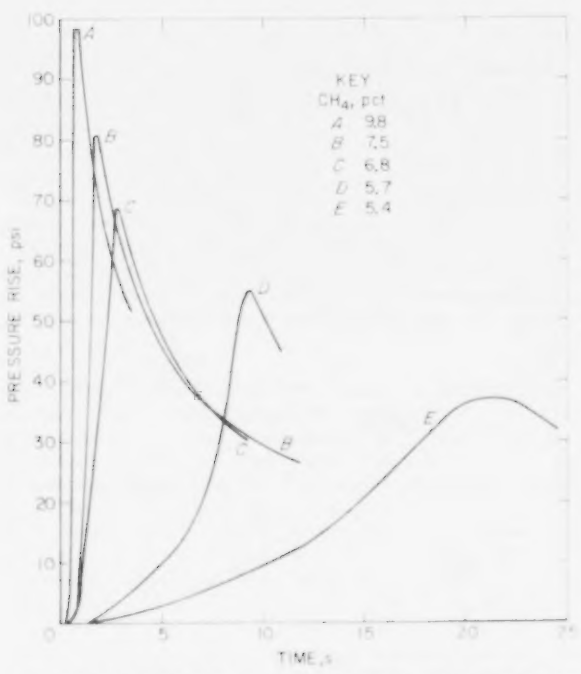


Figure 78.—Explosion pressure growth for methane-air mixtures in 3.65-m (12-ft) diam sphere at 25 C and 1 atm.

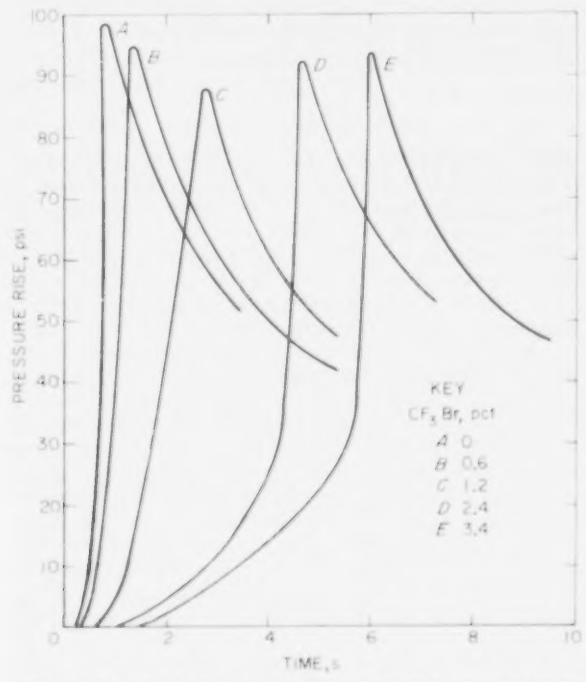


Figure 80.—Explosion pressure growth for 9.5 pct methane-air mixtures and added bromotrifluoromethane (Halon 1301) in 3.65-m (12-ft) diam sphere at 25 C and 1 atm.

Where such explosions are vented, the maximum pressures developed can be limited to a few pounds per square inch or less if the vent area is at least as large as the cross-sectional area of the particular enclosure. The following expression derived by Bureau investigators (*92*) predicts the unrestricted venting requirements for ignitions of hydrocarbon vapor-air-nitrogen mixtures in large spherical or cubical enclosures:

$$A = 13.03 \times 10^{-3} V^{2/3} (E-1) S_u / c_d \left(\frac{E \rho_u}{P-P_o} \right)^{1/2} \quad (82)$$

where A is vent area (m^2), V is enclosure volume (m^3), E is expansion ratio of combustion products, S_u is mixture burning velocity (cm/sec), c_d is vent discharge coefficient, ρ_u is density of unburned gas mixture (g/cm^3), P_o is initial pressure (psig), and P is vent control pressure (psig). Predicted pressure rise ($P-P_o$) as a function of the vent ratio ($A/V^{2/3}$) is shown in figure 81 for methane-air ignitions with 0 to 30 pct added nitrogen; a c_d value of 0.8 is assumed. The calculated venting requirements are most reliable for enclosures with a length-diameter ratio close to unity and are at least as conservative as those found experimentally for deflagrations of hydrocarbon-air systems. They are particularly useful in the venting of large enclosures or buildings which can tolerate at most a few pounds per square inch of overpressure before structural failure.

Rasbash (*86*) developed the following expression for venting large buildings using propane-air mixtures:

$$P_m = 1.5\ P_v + 0.5\ K;\ K = 1 \text{ to } 5 \quad (83)$$

where P_m (psi) is maximum pressure during venting, P_v (psi) is pressure when venting starts, and K is ratio of smallest cross-sectional area of building to total vent area. The expression is limited to building length-width ratios of up to 3 and vent materials that rupture or open below 1 psi. For venting ducts, the maximum pressure (P_m, psi) is given by

$$P_m = 1.8\ K \quad ;\ K = 2 \text{ to } 32 \quad (84)$$

$$P_m = 0.35\ L/D + 0.9\ K;\ K = 1 \text{ to } 2 \quad (85)$$

where L/D is length-diameter ratio of duct and K is ratio of duct cross-sectional area to vent area. These equations were derived by Rasbash (*85*) and limited to unobstructed ducts, gas mixture flame speeds of less than 3 m/s, and L/D ratios between 6 and 30; higher pressures result with obstructed ducts. In both ducts and buildings or enclosures, the maximum pressure will tend to be minimal when the area vent ratio (K) is unity or less.

In vented and unvented systems, explosion pressures will be greater with turbulent mixtures than with quiescent ones. On the other hand, the explosion pressure hazard is greatly reduced when the mixture is of borderline flammability and only capable of upward flame propagation. Furno's data (*22*) for lean H_2-air mixtures (fig. 82) and rich C_4H_{10}-air mixtures (fig. 83) are classic examples; note that pressure rises are minimal until fuel concentrations are capable of both upward and downward propagation. In comparison, lean CH_4-air or CO-air mixtures do not have greatly different upward limits and downward limits of propagation. Burgess (*5*) found such trends consistent with preferential diffusion effects and showed the stoichiometric ratio of upward-downward limits to correlate with the square root ratio of the oxygen-fuel diffusivities.

Gaseous detonations may be assumed to produce explosion pressures of about twice the values for constant-volume deflagrations (equation 52) and maximum pressure rise ratios (P_2/P_1) of about 18:1; reflected pressures are higher but are not greatly destructive because of their very short duration. Container failures due to detonations will be typically characterized by fine fragmentation of brittle materials, shear or hoop stress failures of ductile materials, "peeling back" of failed ductile materials as in tube failures, and relatively far field damage due to flying fragments and blast waves. Blast wave damage is treated in the next section. One should understand that gaseous deflagrations at high pressures can produce localized material damage that can be as severe as that of gaseous detonations.

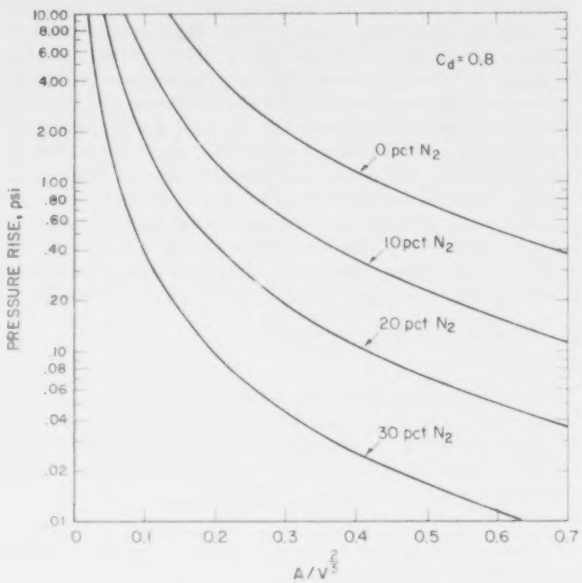


Figure 81.—Calculated pressure rise versus vent ratio ($A/V^{2/3}$) for stoichiometric methane-air ignitions with 0, 10, 20, and 30 pct added nitrogen at 25° C and 1 atm.

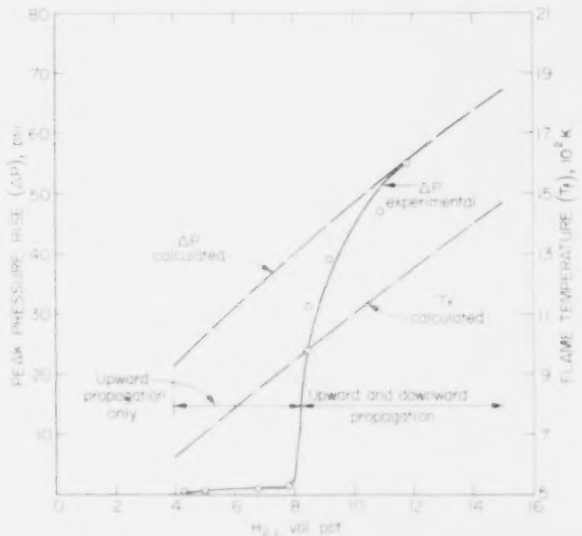


Figure 82.—Peak pressure rises and flame temperatures for H_2-air mixtures in 3.65-m (12-ft) diam sphere at 25° C and 1 atm.

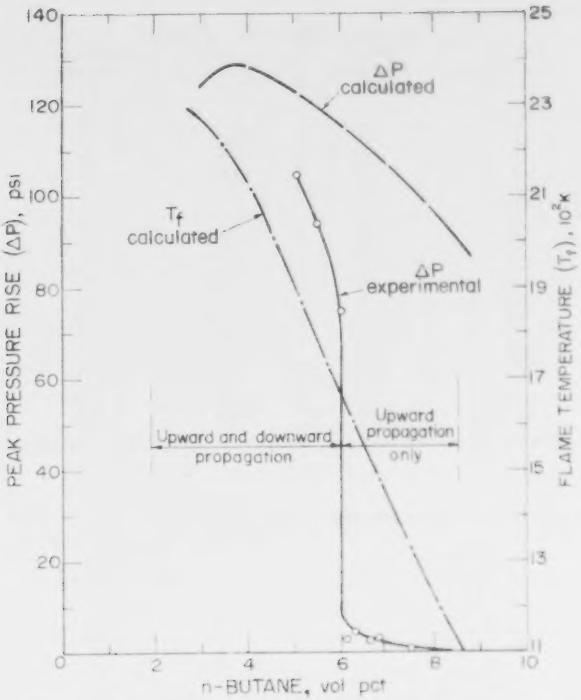


Figure 83.—Peak pressure rises and flame temperatures for C_4H_{10}-air mixtures in 3.65-m (12-ft) diam sphere at 25° C and 1 atm.

BLAST WAVE CRITERIA

The blast wave pressures from weakly confined gaseous deflagrations are small because a large fraction of the available chemical energy is not converted to pressure energy before the container walls fail (see equation 56). In such cases, any pressure energy will be largely dissipated by convection, and the TNT equivalent will be small and not very meaningful. In the case of strongly confined gaseous deflagrations and particularly detonations, their blast pressure energy and TNT equivalence will tend to approximate the energy yield given by their heats of combustion (ΔH_c). By application of the cube root scaling law (equation 55), the blast overpressures of TNT charges are normally plotted as a function of a scaled distance (λ),

$$\lambda = d/W^{1/3}, \qquad (86)$$

where d is distance (ft) and W is charge weight (lb). Figure 84 shows the plot obtained by Kingery (*45*); the peak overpressures refer to the static or side-on pressures of the blastwave. Thus, if a combustible mixture has a TNT equivalence of 454 g (1 lb), the peak overpressure (static) would be approximately 10 psi at a distance of 3.1 m (10 ft); the theoretical chemical energy of the mixture or equivalent TNT (1,100 cal/g) would be 499 kcal (454 g × 1,100 cal/g). Detonation properties of TNT and other explosives are summarized in table 47 (*63*); the listed heat of detonation for TNT (1,400 cal/g) is a high value because of a high TNT density and assumption of condensed $H_2O(l)$ in the explosion products.

Blast wave damage that may occur to structural materials or buildings is given in table 48 (*26*, p. 163) in terms of peak overpressure and in table 49 (*19*) as a function of scaled distance (λ). Figure 84 can be invoked to assess the damage potential in each case as a function of both overpressure and scaled distance relative to TNT. It is important to note in table 48 that most ordinary constructional materials can fail with only a few pounds per square inch overload; these values refer to external pressure loading but can even be lower for internal loading, as in a vessel explosion. Other data by the same author (*26*, p. 253) indicated that an average sized aircraft would suffer severe damage at a blast overpressure of approximately 3 psi and only light damage at 1 psi. With any structural material, the greatest pressure damage will occur to components of minimum thickness and maximum width or length without any material supports or reinforcement.

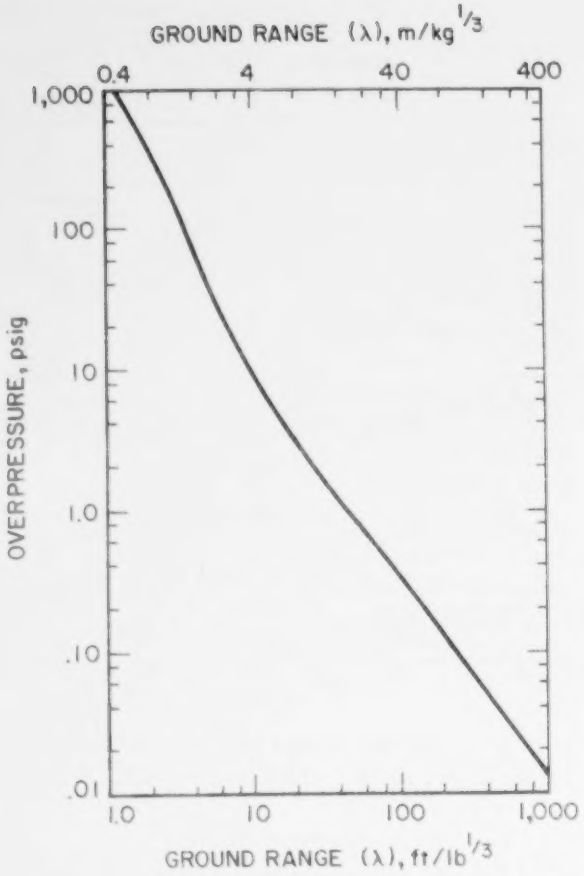


Figure 84.—Peak overpressure versus scaled distance (λ) for hemispherical TNT surface bursts.

Biological effects of blast overpressures by Richmond (*87*) are included in figure 85. Note that the lethal overpressure values are for a 400-ms pulse duration and that about 50 psig would be lethal at a 50-pct probability level for a human or animal target. However, since the biological damage is impulse sensitive, the values for both lethal and other biological damage will vary with the pressure pulse duration. Accordingly, the indicated overpressures for biological damage can be substantially greater when the pulse duration is of much shorter duration than 400 ms.

Table 47. — Properties of explosives (*63*)

Explosive	Molecular weight	Nominal density, g/cm³	Heat of[1] detonation, cal/g	Detonation velocity, m/s	Detonation[1] pressure, kbar
PRIMARY HIGH EXPLOSIVES					
Lead azide, PbN_6	291.3	4.8	367	5,180	NA
Lead styphnate, $PbC_6HN_3O_8$	450.3	3.1	457	5,200	NA
Mercury fulminate, $C_2N_2O_2Hg$	284.6	4.4	427	5,000	NA
SECONDARY HIGH EXPLOSIVES					
Baratol, 24 pct TNT + 76 pct Ba $(NO_3)_2$	NA	2.55	560	4,870	140
Comp B, 36 pct TNT + 63 pct RDX	NA	1.72	1,530	7,990	295
LX-04-1, 85 pct HMX + 15 pct Viton A	NA	1.86	1,420	8,460	360
Nitrocellulose, guncotton (≥13.35 pct N)	274.1	1.20	1,260	7,300	210
Nitroglycerine, propanetriol trinitrate	227.1	1.60	1,590	7,700	253
Nitromethane	61.0	1.13	1,940	6,320	140
PETN, pentaerythritol tetranitrate	316.2	1.76	1,650	8,300	305
Pentolite, 50 pct TNT + 50 pct PETN	NA	1.67	1,520	7,470	248
RDX, Trinitrotriazacyclohexane	222.1	1.77	1,620	8,640	338
Tetranitromethane	196.0	1.65	550	NA	144
Tetryl, trinitrophenylmethylnitramine	287.0	1.71	1,520	7,850	250
TNT, trinitrotoluene	227.1	1.64	1,400	6,930	220

[1]Calculated or observed values; heats of detonation refer to maximum calculated values with water formed as liquid; detonation pressures refer to Chapman-Jouguet state.

Table 48. — Peak overpressures for failure of structural materials (*26*, p. 163)

Structural material	Usual failure	Peak blast overpressure, psi
Glass windows	Shattering	0.5-1.0
Corrugated asbestos siding	Shattering	1.0-2.0
Corrugated steel or aluminum paneling	Connection failure and buckling	1.0-2.0
Wood siding panels (standard house construction)	Connection failure and buckling	1.0-2.0
Concrete or cinderblock walls, 8 or 12 in thick (not reinforced)	Shattering	2.0-3.0
Brick walls, 8 or 12 in thick (not reinforced)	Shearing and flexure failures	7.0-8.0

Table 49. — Scaled distance for building damage from statistical survey of chemical explosions (*19*)

Category	Building damage	Scaled distance (λ)	
		$ft\,lb^{1/3}$	$m\,kg^{1/3}$
A	Demolished, not standing	7.4	2.9
B	Severe damage; standing but substantially destroyed, some walls gone	16.6	6.6
C	Moderate damage; walls bulged, roof cracked or bulged, studs and rafters broken	25.0	9.9
D	Slight damage; doors, sashes, or frames removed; plaster or wallboard broken; shingles or siding off	28.1	11.2
E	Minor damage to glass or miscellaneous small items (similar to that resulting from high wind)	42.7	17.0

An overpressure of 1 psi is reported by Glasstone (*26*) for knocking over a human body but again would be overly conservative for combustible explosions where pressure pulse durations are relatively short.

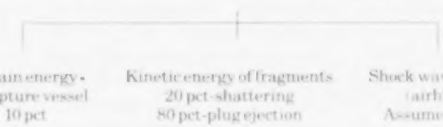
CRATER AND MISSILE CRITERIA

Ground craters can result only from high-energy explosions, as with solid or condensed-phase explosives that are detonated near the ground surface. By the cube root scaling law, the crater diameter (d) is given by

$$d = d_o W^{1/3}, \qquad (87)$$

where W is charge weight and d_o is scaled diameter for a unit weight of the reference explosive. According to Van Dolah (*101*), d_o is approximately 1.5 for a 1-lb charge of TNT with the diameter dimensions in feet. The crater dimensions will depend upon the physical nature of the ground surface and depth of the exploding charge. The crater depth is nominally 1/4 the crater diameter. Many potentially explosive materials such as black powder, smokeless gun propellants, and even ammonium nitrate do not readily detonate and form craters. However, both ammonium nitrate and black powder are capable of detonation and crater formation when they are combusted in massive quantities under high degrees of confinement or with a high explosive ignition stimulus.

Missile damage from the fragmentation of a vessel involving gaseous explosions will depend upon the mass, shape, and velocity of the fragment(s) and the nature of the target material. In such assessments, it is often necessary to assume what fraction of the available chemical energy (strong confinement) or pressure energy (weak confinement) will be converted into kinetic energy ($E = 1/2\ mv^2$) for propelling the fragment; the average velocity (v) of the fragment (gravitational mass m) can then be calculated. High (*33*) gives the following guidelines for estimating the distribution of available energy:


"Chemical" or "pressure" energy
Strain energy - to rupture vessel 10 pct
Kinetic energy of fragments 20 pct-shattering 80 pct-plug ejection
Shock wave energy (airblast) Assume 100 pct

In practice, the pressure energy for estimating kinetic energies gives more realistic values than the chemical energy when the vessel shatters before maximum explosion pressures are realized. Chemical energy refers to theoretical

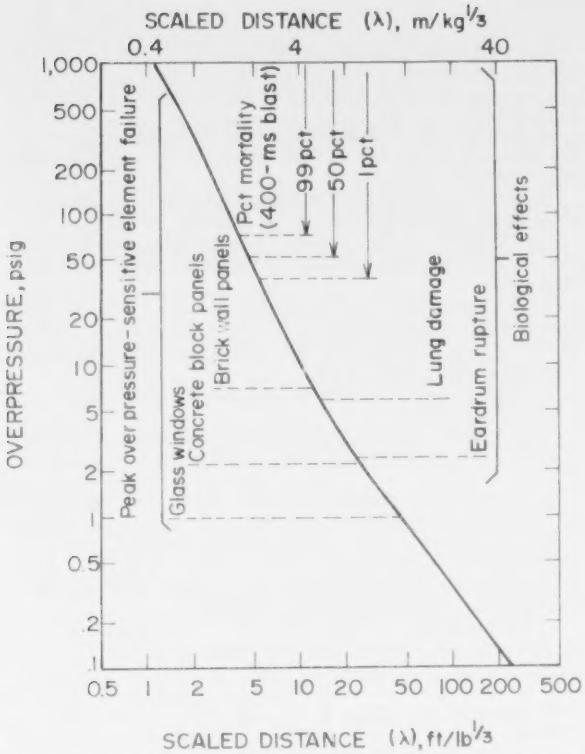


Figure 85.—Peak overpressure and approximate material and biological damage effects from hemispherical TNT surface bursts.

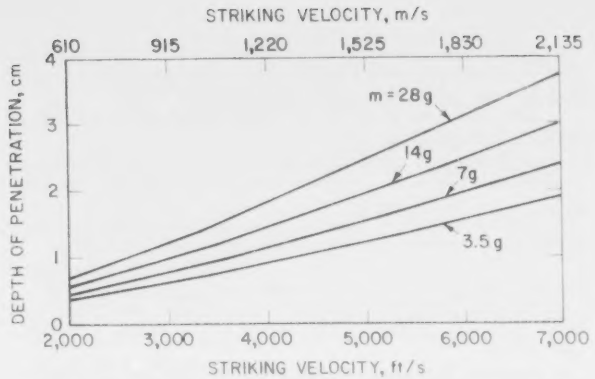


Figure 86.—Depth of penetration of mild steel versus striking velocity for steel fragments of various weights.

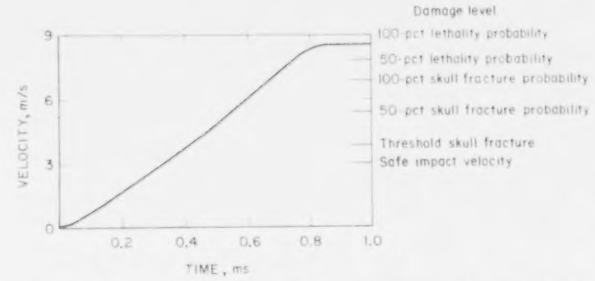


Figure 87.—Velocity-time profile and potential biological damage levels for head or body impacts.

heats of combustion (ΔH_c) or detonation, and pressure energy refers to calculated work outputs (W) assuming adiabatic expansion of products to atmospheric pressure, as given by equation 56,

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

The initial velocity (v_o) of an explosion fragment can be estimated from its distance from the exploding vessel, which is its range (R). From equations of motion, the maximum range is obtained when the trajectory angle (α) of the missile is 45°:

$$R = \frac{v_o^2 \sin 2\alpha}{g}; \qquad (88)$$

also, the maximum height (h) is

$$h = \frac{v_o^2 \sin^2\alpha}{2g}, \qquad (89)$$

where g is the gravitational constant (980 cm/s^2 or 32 ft/s^2). The final or striking velocity of the fragment will be less than v_o because of air drag effects, which are greatest for materials with the largest face areas; this effect will be noticeable over small trajectory ranges.

A useful equation (Demarre's) for predicting the penetration of irregular steel fragments into mild steel plates or similar targets is

$$P_d = kW^{1/3}\left(\frac{v}{1000}\right)^{4/3} \qquad (90)$$

where k is 0.112 for mild steel when the dimensions of the penetration depth (P_d, in), fragment weight (W, oz), and striking velocity (v, ft/s) are in the specified English units. Figure 86 (*84*) shows the predicted values by this equation for fragment weights of 1/8 oz (~3.5 g) to 1 oz (~28 g). The velocity range of 2,000 to 3,000 ft/s (~600 to 900 m/s) is comparable to the muzzle velocity of a 30-caliber rifle weapon. Compared to a concrete-type target, steel may be considered to offer about 10 times greater penetration resistance (*101*).

Human targets have low impact-velocity thresholds for biological damage. Figure 87 (*87*) compares the blast-induced translational velocities of a nylon sphere (1/8-in diam) with various velocity damage thresholds that can result from head or total body impacts; the sphere data reflect the velocity change for the impacts. Of particular significance is that the threshold impact velocity is only about 15 ft/s (~4.5 m/s) for a skull fracture and 30 ft/s (~9 m/s) for a 100-pct lethal probability. Because of many uncertainties in making such correlations, the human damage levels should not be considered as precise values but as approximate values that are generally on the conservative side on the basis of available data.

In the case of cased explosives, the prediction of kinetic energy velocities is complicated by the distribution of energy to the case material and the explosive products. The conversion of available energy to kinetic energy is much greater than in gaseous deflagrations and can be 60 pct or so. Damage by explosives, which is beyond the scope of this report, has been summarized by Van Dolah and other Bureau investigators (*101*).

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APPENDIX A. — SUMMARY OF COMBUSTION PROPERTIES OF LIQUID AND GASEOUS COMPOUNDS[1] (GASEOUS COMBUSTION IN AIR AT ATMOSPHERIC PRESSURE)

Combustible	Formula	Mol wt	Sp gr (air = 1)	BP, °C	C_{st} (in air), vol pct	ΔH_f (25° C), kcal/mol	ΔH_c (net, 25° C), kcal/mol	Flash-point, °C	Minimum AIT, °C	Flammable limits	
										L_{25}, vol pct	U_{25}, vol pct
PARAFFINIC HYDROCARBONS (STRAIGHT-CHAIN ALKANES)											
Methane	CH_4	16.04	0.55	−164	9.48	−17.9	191.8	[2] −188	630	5.0	15.0
Ethane	C_2H_6	30.07	1.04	−89	5.65	−20.2	341.3	[2] −135	515	3.0	12.4
Propane	C_3H_8	44.11	1.52	−42	4.02	−24.8	488.5	[2] −104	450	2.1	9.5
n-Butane	C_4H_{10}	58.12	2.01	−.5	3.12	−30.2	635.4	[2] −74	370	1.8	8.4
n-Pentane	C_5H_{12}	72.15	2.49	36	2.55	−35.0	782.0	[2] −49	260	1.4	7.8
n-Hexane	C_6H_{14}	86.18	2.98	69	2.16	−40.0	928.9	−23	225	1.2	7.4
n-Heptane	C_7H_{16}	100.21	3.46	98	1.87	−44.9	1,075.8	−3	225	1.1	6.7
n-Octane	C_8H_{18}	114.23	3.94	126	1.65	−49.8	1,222.8	14	220	.95	[3]6.5
n-Nonane	C_9H_{20}	128.26	4.43	151	1.47	−54.7	1,369.7	31	205	[4].85	NA
n-Decane	$C_{10}H_{22}$	142.29	4.91	174	1.33	−59.7	1,516.6	46	210	[4].75	[5]5.6
n-Dodecane	$C_{12}H_{26}$	170.33	5.88	215	1.12	−69.5	1,810.5	74	204	[2].60	NA
n-Tetradecane	$C_{14}H_{30}$	198.38	6.85	253	.97	−79.4	2,104.3	107	200	[2].50	NA
n-Hexadecane	$C_{16}H_{34}$	226.45	7.82	287	.85	−89.2	2,398.2	[2]126	205	[2].43	NA
PARAFFINIC HYDROCARBONS (BRANCHED-CHAIN ALKANES)											
2-Methylpropane (isobutane)	C_4H_{10}	58.12	2.07	−12	3.12	−32.2	634	[2] −81	460	1.8	8.4
2-Methylbutane (isopentane)	C_5H_{12}	72.15	2.49	28	2.55	−36.9	780	< −50	420	1.4	7.6
2-Methylpentane	C_6H_{14}	86.18	3.0	60	2.16	−41.7	927	NA	306	1.2	7.0
2,2-Dimethylpropane (neopentane)	C_5H_{12}	72.15	2.5	10	2.55	−39.7	777	NA	450	1.4	7.5
2,2-Dimethylbutane	C_6H_{14}	86.18	3.0	50	2.16	−44.4	925	−48	425	1.2	7.0
2,3-Dimethylpentane	C_7H_{16}	100.21	3.5	90	1.87	−47.6	1,073	NA	335	1.1	6.8
2,2,3-Trimethylbutane	C_7H_{16}	100.21	3.46	81	1.87	−49.0	1,072	NA	420	1.0	NA
2,2,4-Trimethylpentane (isooctane)	C_8H_{18}	114.23	3.9	99	1.65	−53.6	1,219	−12	415	.95	6.0
2,2,3,3-Tetramethylpentane	C_9H_{20}	128.26	4.4	134	1.47	−56.7	1,368	NA	430	.80	[6]4.9
3,3-Diethylpentane	C_9H_{20}	128.26	4.4	146	1.47	−55.4	1,369	NA	290	[7].70	[6]5.7
UNSATURATED HYDROCARBONS (ALKENES AND DIENES)											
Ethylene (ethene)	C_2H_4	28.05	0.97	−104	6.53	12.5	316.2	NA	490	2.7	36
Propylene (propene)	C_3H_6	42.08	1.45	−47	4.45	4.9	460.4	NA	460	2.4	11
α-Butylene (1-butene)	C_4H_8	56.12	1.94	−6.3	3.37	−.03	607.7	NA	385	1.6	10
β-Butylene (2-butene)	C_4H_8	56.12	1.94	3.7	3.37	−1.7	606.0	NA	325	1.7	9.7
n-Amylene (1-pentene)	C_5H_{10}	70.14	2.42	30	2.72	−5.0	754.3	−18 oc	275	1.4	8.7
3-Methyl-1-butene	C_5H_{10}	70.14	2.42	20	2.72	−6.9	752.3	NA	365	1.5	9.1
Propadiene (allene)	C_3H_4	40.07	1.38	−35	4.97	45.9	443.7	NA	NA	2.2	NA
1,3-Butadiene	C_4H_6	54.09	1.87	−4.4	3.67	26.3	576.3	NA	420	2.0	12
2-Methyl-1,3-butadiene (isoprene)	C_5H_8	68.11	2.40	34	2.90	18.1	720	−54	460	2.0	9
UNSATURATED HYDROCARBONS (ACETYLENES)											
Acetylene (ethyne)	C_2H_2	26.04	0.91	−84	7.73	54.2	300.1	NA	305	2.5	100
Methylacetylene (propyne)	C_3H_4	40.07	1.40	−23	4.97	44.3	442.1	NA	340	1.7	NA
CYCLIC HYDROCARBONS (SATURATES)											
Cyclopropane (trimethylene)	C_3H_6	42.08	1.45	−33	4.45	12.7	465	[2]92	500	2.4	10.4
Cyclobutane	C_4H_8	56.12	1.94	12	3.37	6.4	614	NA	NA	1.8	NA
Cyclopentane	C_5H_{10}	70.14	2.42	49	2.72	−18.5	740.8	NA	380	1.5	NA
Cyclohexane	C_6H_{12}	84.16	2.91	81	2.27	−29.4	881.7	−20	245	1.3	7.8
Cycloheptane	C_7H_{14}	98.19	3.39	118	1.96	−28.5	1,034	NA	NA	1.1	6.7
Ethylcyclobutane	C_6H_{12}	84.16	2.91	71	2.27	NA	880	NA	210	1.2	7.7
Ethylcyclopentane	C_7H_{14}	98.19	3.39	104	1.96	−30.4	1,033	NA	260	1.1	6.7
Methylcyclohexane	C_7H_{14}	98.19	3.39	101	1.96	−37.0	1,026	−4	250	1.1	6.7
Ethylcyclohexane	C_8H_{16}	112.21	1.71	132	1.71	−41.1	1,174	35	260	[8].95	[8]6.6
Diethylcyclohexane	$C_{10}H_{20}$	140.26	NA	174	1.38	NA	NA	49	240	[3].80	[7]6.0
Pinane	$C_{10}H_{18}$	138.26	NA	169	1.42	NA	NA	NA	NA	[9].74	[9]7.2
Bicyclohexyl	$C_{12}H_{22}$	166.31	5.7	238	1.18	−77.6(l)	1,687	74	245	[7].65	[10]5.1
Isopropyl bicyclohexyl	$C_{15}H_{28}$	208.37	NA	283	.94	−54.9(l)	2,165	124	230	[10].52	[11]4.1

See footnotes on page 77.

APPENDIX A. — SUMMARY OF COMBUSTION PROPERTIES OF LIQUID AND GASEOUS COMPOUNDS[1] (GASEOUS COMBUSTION IN AIR AT ATMOSPHERIC PRESSURE) — Continued

Combustible	Formula	Mol wt	Sp gr (air = 1)	BP, °C	C_{st} (in air), vol pct	ΔH_f (25° C), kcal/mol	ΔH_c (net, 25° C), kcal/mol	Flash-point, °C	Minimum AIT, °C	Flammable limits	
										L_{25}, vol pct	U_{25}, vol pct
CYCLIC HYDROCARBONS (UNSATURATES)											
Methylcyclopentadiene	C_6H_8	80.10	NA	NA	2.55	NA	799	49	445	[7]1.3	[7]7.6
Cyclohexene	C_6H_{10}	82.15	2.8	83	2.40	−1.3	852	NA	310	[7]1.2	NA
Dipentene (dl-limonene)	$C_{10}H_{16}$	136.24	4.7	178	1.47	−13.2(l)	1,390	45	237	[10].75	[10]6.1
α-Pinene (turpentine)	$C_{10}H_{16}$	136.24	4.7	156	1.47	−4.1(l)	1,399	33	255	[7].7	NA
AROMATIC HYDROCARBONS (BENZENES)											
Benzene (benzol)	C_6H_6	78.12	2.69	80	2.72	19.8	757.5	−11	560	[7]1.3	[7]7.9
Toluene	C_7H_8	92.15	3.18	111	2.27	12.0	901.5	4	480	[7]1.2	[7]7.1
Ethylbenzene	C_8H_{10}	106.17	3.67	136	1.96	7.1	1,049	15	430	[7]1.0	[7]6.7
o-Xylene (1,2-dimethylbenzene	C_8H_{10}	106.17	3.67	144	1.96	4.5	1,046	32	530	[7]1.1	[7]6.4
m-Xylene	C_8H_{10}	106.17	3.67	139	1.96	4.1	1,046	29	465	[7]1.1	[7]6.4
p-Xylene	C_8H_{10}	106.17	3.67	138	1.96	4.3	1,046	27	530	[7]1.1	[7]6.6
Cumene (isopropylbenzene)	C_9H_{12}	120.20	4.15	152	1.72	.94	1,194	44	425	[7].88	[7]6.5
p-Cymene	$C_{10}H_{14}$	134.22	4.63	177	1.53	−6.9	1,342	47	435	[7].85	[7]6.5
n-Butylbenzene	$C_{10}H_{14}$	134.22	4.6	183	1.53	−3.3	1,342	71	410	[7].82	[7]5.8
sec-Butylbenzene	$C_{10}H_{14}$	134.22	4.6	173	1.53	−4.2	1,341	52	420	[7].77	[7]5.8
tert-Butylbenzene	$C_{10}H_{14}$	134.22	4.6	169	1.53	−5.4	1,340	60	450	[7].77	[7]5.8
Isobutylbenzene	$C_{10}H_{14}$	134.22	4.6	173	1.53	−5.2	1,340	55	430	[7].82	[9]6.0
p-Diethylbenzene	$C_{10}H_{14}$	134.22	4.6	183	1.53	−5.3	1,340	57	430	[7].80	NA
Styrene (vinylbenzene)	C_8H_8	104.16	3.6	145	2.05	35.2	1,019	32	490	[8]1.1	[8]6.1
Methylstyrene	C_9H_{10}	118.18	4.1	163	1.79	28.3	1,164	57 oc	495	[6].7	NA
AROMATIC HYDROCARBONS (POLYNUCLEAR)											
Naphthalene	$C_{10}H_8$	128.19	4.4	218	1.71	36.1	1,208	79	526	[5]0.88	[8]5.9
1-Methylnaphthalene	$C_{11}H_{10}$	142.20	NA	245	1.53	27.9	1,351	NA	530	[2].80	NA
Tetralin (tetrahydronaphthalene)	$C_{10}H_{12}$	132.21	4.6	208	1.58	6.6	1,294	71	385	[7].84	[10]5.0
Decalin (decahydronaphthalene)	$C_{10}H_{18}$	138.25	4.8	196	1.42	−40.4	1,420	57	250	[7].71	[7]4.9
Dimethyl decalin	$C_{12}H_{22}$	166.30	NA	232	1.18	NA	NA	84	235	[7].67	5.4
Diphenyl (biphenyl)	$C_{12}H_{10}$	154.20	5.31	255	1.42	43.5	1,461	113	540	[7].60	[10]5.8
Diphenylmethane (ditane)	$C_{13}H_{12}$	168.24	5.82	264	1.29	21.3(l)	1,591	130	485	[2].70	NA
2-Isopropylbiphenyl	$C_{15}H_{16}$	196.28	NA	269	1.09	11.8(l)	1,883	140	435	[9].53	[11]3.2
Anthracene	$C_{14}H_{10}$	178.24	6.15	340	1.25	55.2	1,661	121	540	[2].65	NA
p-Terphenyl (diphenylbenzene)	$C_{18}H_{14}$	230.31	NA	376	.97	NA	NA	207 oc	535	[2].96	NA
ALCOHOLS (ALKANOLS AND CYCLOALKANOLS)											
Methanol	CH_3OH	32.04	1.11	65	12.25	−48.1	159	11	385	6.7	[3]36
Ethanol	C_2H_5OH	46.07	1.59	79	6.53	−56.1	306	13	365	3.3	[3]19
n-Propanol	C_3H_7OH	60.11	2.07	97	4.45	−61.6	448	25	440	[4]2.2	[7]14
Isopropanol (2-propanol)	C_3H_7OH	60.11	2.1	82	4.45	−61.6	448	12	399	2.2	[7]12
n-Butanol	C_4H_9OH	74.12	2.56	117	3.37	−65.6	596	29	365	[7]1.7	[7]12
sec-Butanol	C_4H_9OH	74.12	2.6	100	3.37	−69.9	595	24	405	[7]1.7	[7]9.8
tert-Butanol	C_4H_9OH	74.12	2.6	82	3.37	−74.7	591	11	480	[7]1.9	[7]9
Isobutanol (2-methyl-1-propanol)	C_4H_9OH	74.12	2.6	108	3.37	−79.7(l)	586	28	427	[7]1.7	[7]11
n-Pentanol (amyl alcohol)	$C_5H_{11}OH$	88.15	3.04	137	2.72	−72.3	742	38	300	[7]1.4	[7]10
tert-Pentanol	$C_5H_{11}OH$	88.15	3.0	102	2.72	−78.7	738	41	435	[2]1.4	NA
Isopentanol (3-methyl-1-butanol)	$C_5H_{11}OH$	88.15	3.0	129	2.72	−85.2(l)	732	43	350	[7]1.4	[7]9
n-Hexanol	$C_6H_{13}OH$	102.18	3.53	158	2.27	−76.4	892	63	300	[7]1.2	NA
Methyl isobutyl carbinol	$C_6H_{13}OH$	102.18	NA	133	2.27	−103.8(l)	865	41	NA	[6]1.0	[6]5.5
Diisobutyl carbinol	$C_9H_{19}OH$	144.26	5.0	176	1.53	NA	NA	74	NA	[7].82	[7]6.1
Cyclohexanol	$C_6H_{11}OH$	100.16	3.5	161	2.40	−70.4	935	68	300	[5]1.2	NA
1-Methyl cyclohexanol	$C_7H_{13}OH$	114.19	3.9	155	2.05	−88.2(l)	975	65	295	[5]1.0	NA
ALCOHOLS (GLYCOLS)											
Ethylene glycol (1,2-ethanediol)	$C_2H_4(OH)_2$	62.07	2.14	198	7.73	−93.1	268	111	400	[2]3.5	NA
Propylene glycol	$C_3H_6(OH)_2$	76.11	2.52	189	4.97	−119.3(l)	394	99	410	[5]2.6	[6]12.5
Trimethylene glycol	$C_3H_6(OH)_2$	76.11	2.6	214	4.97	NA	NA	NA	400	[2]1.7	NA
Tetramethylene glycol	$C_4H_8(OH)_2$	90.12	NA	235	3.67	NA	NA	NA	390	NA	NA
βButylene glycol	$C_4H_8(OH)_2$	90.12	3.1	204	3.67	−122.9(l)	542	121	395	[2]1.9	NA
Pentamethylene glycol	$C_5H_{10}(OH)_2$	104.15	NA	260	2.90	−105.1(l)	712	129	335	NA	NA

Combustible	Formula	Mol wt	Sp gr (air = 1)	BP, °C	C_{st} (in air), vol pct	ΔH_f (25° C), kcal/mol	ΔH_c (net, 25° C), kcal/mol	Flash-point, °C	Minimum AIT, °C	Flammable limits	
										L_{25}, vol pct	U_{25}, vol pct
ALCOHOLS (GLYCOLS) — continued											
Triethylene glycol	$C_6H_{12}O_2(OH)_2$	150.17	5.17	278	2.72	−191.4(l)	777	156	371	[10]0.9	[9]9.2
Glycerol (1,2,3-propanetriol)	$C_3H_5(OH)_3$	92.11	3.17	290	5.65	−159.8(l)	354	160	370	NA	NA
ALCOHOLS (UNSATURATES AND AROMATICS)											
Propargyl alcohol (2-propynol)	C_3H_3OH	56.07	1.93	114	5.65	10.1	408	36 oc	NA	[4]2.2	[7]14
Allyl alcohol (2-propenol)	C_3H_5OH	58.08	2.0	97	4.97	−31.6	424	21	378	2.5	18
Aldol (3-hydroxybutanal)	$C_2H_4OHC_2H_3O$	88.12	3.0	NA	4.02	−102.9(l)	504	66 oc	250	[2]2.0	NA
Furfuryl alcohol	$CH_2OHC_4H_3O$	98.10	3.4	171	3.67	−66.1(l)	578	75 oc	390	[3]1.8	[7]16
Phenol (carbolic acid)	C_6H_5OH	94.11	3.2	182	2.90	−23.0	715	79	NA	NA	NA
Benzyl alcohol	C_7H_7OH	108.15	3.72	205	2.40	−38.5(l)	851	101	436	NA	NA
m-Cresol (3-methylphenol)	C_7H_7OH	108.15	3.7	202	2.40	−31.6	858	94	559	[10]1.1	NA
ETHERS (ALKYLS)											
Methyl ether (dimethyl ether)	$(CH_3)_2O$	46.07	1.59	−23	6.53	−44.0	316	NA	350	3.4	27
Methyl ethyl ether	$CH_3OC_2H_5$	60.10	2.1	11	4.44	−51.7	462	−37	190	2.0	10
Ethyl ether (diethyl ether)	$C_2H_5)_2O$	74.12	2.56	35	3.37	−60.3	605	−45	160	1.9	36
Ethyl propyl ether	$C_2H_5OC_3H_7$	88.15	3.28	64	2.72	NA	750	−20	NA	1.7	9
Isopropyl ether	$(C_3H_7)_2O$	102.18	3.53	68	2.27	−76.2	893	−28	NA	1.4	7.9
Butyl ether	$(C_4H_9)_2O$	130.22	4.5	142	1.72	−79.8	1,193	25	194	1.5	[6]7.6
Amyl ether (dipentyl ether)	$(C_5H_{11})_2O$	158.29	5.5	190	1.38	−82.5(l)	1,494	57 oc	170	[2]1.7	NA
Hexyl ether	$(C_6H_{13})_2O$	186.34	5.5	223	1.15	NA	NA	77 oc	185	[2]1.6	NA
ETHERS (UNSATURATES AND MISCELLANEOUS)											
Ethylene oxide (epoxyethane)	C_2H_4O	44.05	1.5	14	7.72	−12.6	291	NA	429	3.6	100
Propylene oxide	C_3H_6O	58.08	2.0	34	4.97	−22.2	433	−37	464	2.8	37
Methyl vinyl ether	$CH_3OC_2H_3$	58.08	2.0	12	4.97	NA	411	NA	287	2.6	39
Vinyl ether (diethenyl ether)	$(C_2H_3)_2O$	70.09	2.42	28	4.02	−3.0	547	NA	360	1.7	27
Furan (epoxybutadiene)	C_4H_4O	68.07	2.3	31	4.44	−8.3	484	NA	NA	2.3	14.3
Tetrahydrofuran (epoxybutane)	C_4H_8O	72.10	2.5	67	3.67	−44.0	563	−14	321	2.0	NA
p-Dioxane (diethylene dioxide)	$(C_2H_4O)_2$	88.12	3.0	101	4.02	−75.3	532	12	265	2.0	22
Trioxane (metaformaldehyde)	$(CH_2O)_3$	90.08	NA	115	6.53	−124.4(s)	331	45 oc	414	[6]3.6	[6]29
Acetal	$C_2H_4(OC_2H_5)_2$	118.18	4.1	103	2.40	−117.2(l)	852	37	230	1.6	10
Phenyl ether	$(C_6H_5)_2O$	170.21	5.86	258	1.47	−3.5(l)	1,414	115	620	[2]1.8	NA
ETHERS (CELLOSOLVES)											
Methyl cellosolve (2-methoxyethanol)	$CH_3OC_2H_4OH$	76.11	2.6	125	4.97	−114.8	399	46	380	[8]2.5	[10]20
Ethyl cellosolve	$C_2H_5OC_2H_4OH$	90.12	3.0	135	3.67	NA	NA	94	235	[6]1.8	[6]14
Butyl cellosolve	$C_4H_9OC_2H_4OH$	118.18	4.08	171	2.40	NA	NA	71	245	[10]1.1	[9]11
ALDEHYDES (ALKYLS)											
Formaldehyde (methanal)	HCHO	30.03	1.0	−20	17.32	−27.7	124	NA	430	7.0	73
Acetaldehyde (ethanal)	CH_3CHO	44.05	1.52	21	7.73	−39.8	264	−38	175	4.0	60
Propionaldehyde	C_2H_5CHO	58.08	2.01	49	4.97	−45.9	409	−7 oc	207	2.9	17
Butyraldehyde	C_3H_7CHO	72.12	2.5	76	3.67	−49.0	558	−7	230	2.5	12.5
ALDEHYDES (MISCELLANEOUS)											
Acrolein (2-propenal)	C_2H_3CHO	56.07	1.90	53	5.64	−25.1(l)	373	−26	235	2.8	31
Crotonaldehyde (2-butenal)	C_3H_5CHO	70.09	2.4	104	4.02	−34.5(l)	515	13	232	2.1	[3]16
Furaldehyde	$(C_4H_3O)CHO$	96.09	3.3	162	4.02	−46.6(l)	539	60	316	[6]2.1	[6]19.3
Benzaldehyde	C_6H_5CHO	106.13	3.7	178	2.55	−18.5(l)	813	64	192	NA	NA
Paraldehyde (paraacetaldehyde)	$(CH_3CHO)_3$	132.16	4.56	128	2.72	−164.2(l)	747	36 oc	238	1.3	NA
KETONES (ALKYLS)											
Acetone (propanone)	$(CH_3)_2CO$	58.08	2.01	56	4.97	−52.0	403	−18	465	2.6	13
Methyl ethyl ketone (2-butanone)	$CH_3COC_2H_5$	72.12	2.49	80	3.67	−57.0	548	−6	516	1.9	11

See footnotes on page 77.

APPENDIX A. — SUMMARY OF COMBUSTION PROPERTIES OF LIQUID AND GASEOUS COMPOUNDS[1] (GASEOUS COMBUSTION IN AIR AT ATMOSPHERIC PRESSURE) — Continued

Combustible	Formula	Mol wt	Sp gr (air = 1)	BP, °C	C_{st} (in air), vol pct	ΔH_f (25° C), kcal/mol	ΔH_c (net, 25° C), kcal/mol	Flash-point, °C	Minimum AIT, °C	Flammable limits	
										L_{25}, vol pct	U_{25}, vol pct
KETONES (ALKYLS) — continued											
Diethyl ketone (3-pentanone)	$(C_2H_5)_2CO$	86.14	2.97	102	2.90	−61.8	692	13 oc	450	1.6	NA
Methyl propyl ketone	$CH_3COC_3H_7$	86.14	2.97	102	2.90	−61.8	692	7	505	1.6	8.2
Methyl butyl ketone	$CH_3COC_4H_9$	100.16	3.46	128	2.40	−78.9	840	35 oc	533	[4]1.2	[7]8
Methyl isobutyl ketone	$CH_3COC_4H_9$	100.16	3.5	117	2.40	−92.9(l)	818	23	460	1.4	7.5
Diisobutyl ketone	$(C_4H_9)_2CO$	142.23	4.9	168	1.59	NA	NA	60	NA	[7]79	[7]6.2
KETONES (MISCELLANEOUS)											
Methyl isopropenyl ketone	$CH_3COC_3H_5$	83.11	2.9	98	3.24	NA	NA	NA	NA	[4]1.8	[4]9
Cyclohexanone	$C_5H_{11}CO$	98.15	3.4	156	2.55	−55.0	798	44	420	[7]1.1	NA
Acetyl acetone (pentanedione)	$(CH_3CO)_2CH_2$	100.13	3.5	139	3.37	−127.6(l)	574	41 oc	340	[2]1.7	NA
Acetophenone (acetylbenzene)	$C_6H_5COCH_3$	120.16	4.1	202	2.16	−20.8	963	82 oc	570	[2]1.1	NA
Isophorone	$C_9H_{14}CO$	138.20	NA	215	1.72	NA	NA	84 oc	460	[6]84	NA
ACIDS (ALKYLS AND AROMATICS)											
Formic acid (methanoic)	HCOOH	46.03	1.6	101	29.53	−90.5	61	[12]69	[12]601	NA	NA
Acetic acid (ethanoic)	CH_3COOH	60.05	2.1	118	9.48	−103.9	200	43	465	[7]5.4	[7]16
Butyric acid (butanoic)	C_3H_7COOH	88.12	3.0	164	4.02	−127.6(l)	480	−72	450	[6]2.0	[6]10
Valeric acid (pentanoic)	C_4H_9COOH	102.13	NA	186	3.12	−117.2	412	96 oc	400	NA	NA
Benzoic acid	C_6H_5COOH	122.13	4.21	249	2.72	−69.4	762	121	570	NA	NA
Adipic acid (hexandioic)	$C_4H_8(COOH)_2$	146.14	5.04	338	3.12	−236.5(s)	617	196	420	[2]1.6	NA
Stearic acid	$C_{17}H_{35}COOH$	284.50	NA	360	.80	−213.1(l)	2,520	196	395	NA	NA
ANHYDRIDES (MISCELLANEOUS)											
Maleic anhydride	$(CHCO)_2O$	98.06	NA	202	6.53	−112.4(s)	322	102	477	[5]1.4	[5]7.1
Acetic anhydride	$(CH_3CO)_2O$	102.09	3.5	140	4.97	−137.6	412	54	390	[4]2.7	[2]10
Phthalic anhydride	$C_6H_4(CO)_2O$	148.12	NA	295	2.72	−110.1(s)	758	152	570	[10]1.2	[11]9.2
ESTERS (ALKYLS)											
Methyl formate (methyl methanoate)	$HCOOCH_3$	60.05	2.07	32	9.48	−83.6	219	−19	465	5.0	23
Ethyl formate	$HCOOC_2H_5$	74.08	2.56	55	5.65	−88.7	367	−20	455	2.8	16
n-Butyl formate	$HCOOC_4H_9$	102.13	3.53	107	3.12	NA	650	18	322	1.7	8.2
Methyl acetate	CH_3COOCH_3	74.08	2.56	57	5.65	−97.9	358	−10	502	3.2	16
Ethyl acetate	$CH_3COOC_2H_5$	88.12	3.04	77	4.02	−105.9(l)	504	−4	427	2.2	11
n-Propyl acetate	$CH_3COOC_3H_7$	102.13	3.53	102	3.12	NA	650	14	450	1.8	[5]8
Isopropyl acetate	$CH_3COOC_3H_7$	102.13	3.5	88	3.12	−124.0(l)	635	4	460	[2]1.7	NA
n-Butyl acetate	$CH_3COOC_4H_9$	116.16	4.01	127	2.55	−126.1(l)	785	22	425	[4]1.4	[7]8
Isobutyl acetate	$CH_3COOC_4H_9$	116.16	4.0	118	2.55	−124.0(l)	787	18	421	2.4	10.5
n-Amyl acetate (pentyl acetate)	$CH_3COOC_5H_{11}$	130.19	4.50	149	2.16	NA	970	25	360	[7]1.0	[7]7.1
Isoamyl acetate	$CH_3COOC_5H_{11}$	130.19	4.5	142	2.16	NA	NA	25	360	[7]1.1	[7]7
Methyl propionate	$C_2H_5COOCH_3$	88.12	3.04	80	4.02	−113.0(l)	494	−2	469	2.4	13
Ethyl propionate	$C_2H_5COOC_2H_5$	102.13	3.53	99	3.12	−114.2(l)	645	12	440	1.8	11
n-Amyl propionate	$C_2H_5COOC_5H_{11}$	144.22	NA	169	1.87	NA	NA	41 oc	380	[2]1.0	NA
Methyl butyrate	$C_3H_7COOCH_3$	102.13	3.52	102	3.12	−119.0(l)	640	14	NA	NA	NA
Ethyl butyrate	$C_3H_7COOC_2H_5$	116.16	4.0	121	2.55	−123.0(l)	788	26	463	NA	NA
n-Butyl stearate	$C_{17}H_{35}COOC_4H_9$	340.60	NA	223	.65	NA	NA	160	355	[2]3	NA
ESTERS (MISCELLANEOUS)											
β-Propiolactone	$C_3H_4CO_2$	72.06	2.5	162	6.53	−67.6	330	74	NA	[3]2.9	NA
γ-Butyrolactone	$C_4H_6CO_2$	86.09	NA	206	4.45	−99.2(l)	450	98 oc	NA	[10]2.0	NA
Vinyl acetate (ethenyl ethanoate)	$CH_3COOC_2H_3$	86.09	3.0	72	4.44	−83.6(l)	466	−8	427	2.6	13.4
Methyl acrylate	$C_2H_3COOCH_3$	86.09	3.0	80	4.44	NA	NA	−3	468	2.8	[6]25
Methyl lactate	$C_2H_4OHCOOCH_3$	104.12	3.6	145	4.45	−152.3(l)	455	49	385	[7]2.2	NA
Ethyl lactate	$C_2H_4OHCOOC_2H_5$	118.13	4.1	155	3.37	−158.6(l)	601	46	400	[7]1.5	NA
Methyl cellosolve acetate	$CH_3COOC_2H_4OCH_3$	118.13	4.1	145	3.37	NA	NA	44	NA	[10]1.7	[6]8.2
Cyclohexylacetate	$CH_3COOC_6H_{11}$	142.20	4.9	174	1.96	NA	NA	58	335	[2]1.0	NA
Benzyl benzoate	$C_6H_5COOC_7H_7$	212.24	7.3	323	1.29	−65.1(s)	1,598	148	480	[3]7	NA

Combustible	Formula	Mol wt	Sp gr (air = 1)	BP, °C	C_{st} (in air), vol pct	ΔH_c (25° C), kcal/mol	ΔH_f (net, 25° C), kcal/mol	Flash-point, °C	Minimum AIT, °C	Flammable limits	
										L_{25}, vol pct	U_{25}, vol pct
AMINES (ALKYLS)											
Methylamine (aminomethane)	CH_3NH_2	31.06	1.1	−6.3	8.52	−5.5	233	NA	430	4.9	20.7
Ethylamine	$C_2H_5NH_2$	45.09	1.6	17	5.29	−11.0	379	NA	385	3.5	14
n-Propylamine	$C_3H_7NH_2$	59.11	2.0	48	3.83	−17.3	525	−37	318	2.0	10.4
n-Butylamine	$C_4H_9NH_2$	73.14	2.5	78	3.01	−22.0	672	−12	312	1.7	[7]1.7 [7]8.9
tert-Butylamine	$C_4H_9NH_2$	73.14	2.5	44	3.01	−28.7	665	NA	380	[7]1.7	
n-Amylamine (aminopentane)	$C_5H_{11}NH_2$	87.16	3.0	103	2.48	NA	NA	7 oc	NA	2.2	NA
Dimethylamine	$(CH_3)_2NH$	45.09	1.6	7.4	5.29	−4.5	386	NA	400	2.8	14.4
Diethylamine	$(C_2H_5)_2NH$	73.14	2.5	56	3.01	−17.3	677	NA	312	1.8	10
Trimethylamine	$(CH_3)_3N$	59.11	NA	2.9	3.83	−5.7	537	NA	NA	2.0	12
Triethylamine	$(C_2H_5)_3N$	101.19	3.5	89	2.10	−23.8	974	7 oc	NA	1.2	8
AMINES (UNSATURATES AND AROMATICS)											
Ethyleneimine (aziridine)	C_2H_4NH	43.07	1.5	56	6.05	29.5	362	−11	320	3.6	46
Allylamine (3-aminopropene)	$C_3H_5NH_2$	57.09	2.0	58	4.22	6.9	491	−29	375	2.2	22
Aniline (phenyl amine)	$C_6H_5NH_2$	93.13	3.2	184	2.63	20.8	787	70	615	[10]1.2	[10]8.3
Diethylaniline	$C_6H_5Ni(C_2H_5)_2$	149.24	5.0	216	1.47	9.6	1,384	85	630	[2]1.8	NA
Biphenylamine	$(C_6H_5)_2NH$	169.23	5.8	302	1.40	48.2	1,495	153	635	[2]1.7	NA
2-Biphenylamine	$C_6H_4NH_2C_6H_5$	169.23	NA	299	1.40	29.1(s)	1,476	NA	450	[2]1.8	NA
AMINES (PYRIDINE DERIVATIVES)											
Pyridine (azine)	C_5H_5N	79.10	2.7	116	3.24	33.5	648	20	482	[3]1.8	[4]12
3-Methyl pyridine (β-picoline)	$C_5H_4(CH_3)N$	93.13	3.2	144	2.63	25.4	792	NA	500	[2]1.4	NA
Quinoline (benzazine)	C_9H_7N	129.16	4.5	238	1.91	35.7(l)	1,084	NA	480	[2]1.0	NA
Nicotine	$C_{10}H_{14}N_2$	162.24	5.6	246	1.53	10.2(l)	1,355	NA	244	[7].75	NA
AMIDES AND CYANIDES											
Hydrogen cyanide	HCN	27.03	0.9	26	14.34	31.2	154	−18	538	5.6	40
Methyl cyanide (acetonitrile)	CH_3CN	41.05	1.4	82	7.08	21.0	296	6 oc	524	4.4	16
Cyanogen	C_2N_2	52.04	NA	−22	9.47	73.8	262	−62	NA	6.6	32
Vinyl cyanide (acrylonitrile)	C_2H_3CN	53.06	1.8	78	5.29	44.2	413	0 oc	481	3.0	17
Dimethyl formamide	$HCON(CH_3)_2$	73.09	2.5	149	4.69	NA	NA	57	435	[7]1.8	[7]14
Acetone cyanohydrin	C_3H_6OHCN	85.11	2.9	NA	3.84	NA	NA	74	687	[6]2.2	[6]12
Acetanilide (phenylacetamide)	$C_6H_5NHCOCH_3$	135.17	4.65	304	2.10	−50.3(s)	962	174 oc	540	[2]1.0	NA
HYDRAZINES											
Hydrazine	N_2H_4	32.05	1.1	114	17.32	22.8	138	38	270	[6]4.7	[6]100
Methylhydrazine	$CH_3N_2H_3$	46.07	1.6	87	7.73	20.4	259	21	185	4.0	NA
1,1-Dimethylhydrazine (UDMH)	$(CH_3)_2N_2H_2$	60.11	2.1	63	4.97	20.3	440	−6	250	2.0	[7]95
NITRATED COMPOUNDS (NITRO ALKYLS AND AROMATICS)											
Nitromethane	CH_3NO_2	61.04	2.1	101	21.83	−17.9	163	35	418	[6]7.3	NA
Nitroethane	$C_2H_5NO_2$	75.07	2.6	115	8.52	−24.2	308	28	414	3.4	NA
1-Nitropropane	$C_3H_7NO_2$	89.09	3.1	131	5.29	−29.8	454	49 oc	421	[6]2.2	NA
2-Nitropropane	$C_3H_7NO_2$	89.09	3.1	120	5.29	−33.5	451	28	428	[6]2.5	NA
Nitrobenzene (nitrobenzol)	$C_6H_5NO_2$	123.11	4.3	211	3.24	3.8(l)	713	88	482	[5]1.8	NA
o-Nitrotoluene	$C_7H_7NO_2$	137.14	4.7	220	2.63	−4(l)	860	106	NA	NA	NA
NITRATED COMPOUNDS (NITRITES AND NITRATES)											
Ethyl nitrite	$C_2H_5NO_2$	75.07	2.6	17	8.52	−24.8	308	−35	90	3.0	50
Ethyl nitrate	$C_2H_5NO_3$	91.07	3.1	87	10.68	−36.8	296	10	NA	4.0	NA
n-Propyl nitrate	$C_3H_7NO_3$	105.10	NA	110	6.05	−41.6	443	20	175	[8]1.8	[8]100
n-Amyl nitrite	$C_5H_{11}NO_2$	117.15	4.0	105	3.01	NA	NA	NA	210	[2]1.0	NA
n-Amyl nitrate	$C_5H_{11}NO_3$	133.15	NA	−155	3.24	NA	NA	52 oc	195	[6]1.1	NA

See footnotes on page 77.

APPENDIX A. — SUMMARY OF COMBUSTION PROPERTIES OF LIQUID AND GASEOUS COMPOUNDS[1] (GASEOUS COMBUSTION IN AIR AT ATMOSPHERIC PRESSURE) — Continued

Combustible	Formula	Mol wt	Sp gr (air = 1)	BP C	C_{st} (in air) vol pct	ΔH_c (25° C) kcal/mol	ΔH_c (net, 25° C) kcal/mol	Flash-point C	Minimum AIT C	Flammable limits	
										L_{25} vol pct	U_{25} vol pct
CHLORINATED COMPOUNDS (ALKYLS)											
Methyl chloride (chloromethane)	CH_3Cl	50.49	1.8	−24	12.25	20.6	153	NA	632	10.7	[7]15.9
Methylene chloride (dichloromethane)	CH_2Cl_2	84.94	2.9	40	17.32	22.8	115	NA	615	[7]15.9	[7]19.1
Ethyl chloride	C_2H_5Cl	64.52	2.2	12	6.52	26.7	299	50	519	3.8	[7]15.4
Ethylene chloride (1,2-dichloroethane)	$C_2H_4Cl_2$	98.96	3.4	83	7.72	31.0	259	13	440	[7]4.5	[7]17.3
Methyl chloroform (trichloroethane)	$C_2H_3Cl_3$	133.41	4.6	74	9.48	24.2	230	NA	485	6.8	NA
n-Propyl chloride	C_3H_7Cl	78.54	2.7	47	4.44	31.1	447	NA	520	2.6	11
Propylene chloride	$C_3H_6Cl_2$	112.99	3.9	96	4.97	39.6	402	16	557	3.4	14.5
n-Butyl chloride	C_4H_9Cl	92.57	3.2	78	3.37	35.2	594	9	250	1.8	[7]10
Isobutyl chloride	C_4H_9Cl	92.57	3.2	69	3.37	38.1	591	NA	NA	2.0	8.8
n-Amyl chloride (chloropentane)	$C_5H_{11}Cl$	106.60	3.7	108	2.72	41.8	740	13 oc	260	[4]1.6	[7]8.6
tert-Amyl chloride	$C_5H_{11}Cl$	106.60	3.7	86	2.72	43.1	738	12	345	[5]1.5	7.4
CHLORINATED COMPOUNDS (UNSATURATES)											
Chloroacetylene	C_2HCl	60.48	NA	−30	9.48	51.1	261	NA	NA	NA	100
Vinyl chloride (chloroethene)	C_2H_3Cl	62.50	2.2	−13	7.99	8.4	276	NA	472	3.6	33
Dichloroethylene (1,2-dichlorethene)	$C_2H_2Cl_2$	96.94	3.4	60	9.47	5	232	6	460	9.7	12.8
Trichloroethylene	C_2HCl_3	131.39	4.5	87	12.25	1.4	210	32	420	12.0	[7]40
Tetrachloroethylene	C_2Cl_4	165.83	5.72	121	17.32	3.4	185	NA	NA	NA	NA
Propargyl chloride (3-chloropropyne)	C_3H_3Cl	74.51	NA	65	7.73	NA	NA	NA	NA	NA	100
Allyl chloride (3-chloropropene)	C_3H_5Cl	76.53	2.6	45	4.97	2	420	32	485	2.9	11
Isopropenyl chloride	C_3H_5Cl	76.53	2.63	23	4.97	NA	NA	NA	NA	4.5	16
Isocrotyl chloride	C_4H_7Cl	90.55	NA	68	3.67	NA	NA	NA	NA	4.2	19
2-Chloro-2-butene	C_4H_7Cl	90.55	3.1	71	3.67	NA	NA	19	NA	2.9	9.3
CHLORINATED COMPOUNDS (ACETYL AND ALCOHOL DERIVATIVES)											
Acetyl chloride	C_2H_3OCl	78.50	2.7	51	9.48	58.3	210	4	390	[2]5.0	NA
Ethylene chlorohydrin (2-chloroethanol)	C_2H_4ClOH	80.52	2.78	128	7.73	70.3(l)	256	60 oc	425	[6]4.9	[6]15.9
CHLORINATED COMPOUNDS (BENZENES)											
Chlorobenzene	C_6H_5Cl	112.56	3.9	132	2.90	12.4	714	29	640	1.4	7.1
Benzyl chloride (chlorotoluene)	C_7H_7Cl	126.59	4.4	179	2.40	16.8(l)	837	67	585	[5]1.1	NA
o-Dichlorobenzene	$C_6H_4Cl_2$	147.01	5.1	181	3.12	7.2	673	66	648	[5]2.2	[5]9.2
BROMINATED COMPOUNDS (ALKYLS)											
Methyl bromide (bromomethane)	CH_3Br	94.94	3.3	3.6	12.24	−9.0	152	NA	537	10	15
Ethyl bromide	C_2H_5Br	108.97	3.8	38	6.52	−15.3	297	NA	511	6.7	11.3
n-Propyl bromide	C_3H_7Br	123.00	4.3	71	4.45	−21.0	443	NA	490	NA	NA
n-Butyl bromide	C_4H_9Br	137.03	4.7	102	3.37	−25.7	590	18	265	[2]2.5	[7]6.6
n-Amyl bromide (bromopentane)	$C_5H_{11}Br$	151.05	NA	130	2.72	−30.9	737	32	NA	NA	NA
BROMINATED COMPOUNDS (UNSATURATES AND BENZENES)											
Propargyl bromide (3-bromopropyne)	C_3H_3Br	118.97	4.1	88	5.65	40	389	10	324	3.0	100
Allyl bromide (3-bromopropene)	C_3H_5Br	120.98	4.2	70	4.97	11.8	418	−1	295	4.4	7.3
Isocrotyl bromide	C_4H_7Br	135.00	NA	NA	3.67	NA	NA	NA	NA	6.4	12
Bromobenzene	C_6H_5Br	157.02	5.4	156	2.90	25.1	713	51	565	[2]1.6	NA
SULFUR COMPOUNDS											
Hydrogen sulfide	H_2S	34.08	1.18	61	12.25	−4.8	124	NA	260	4.0	44
Carbon disulfide	CS_2	76.14	2.63	46	6.53	28.0	252	30	100	1.3	50
Methyl mercaptan (methanethiol)	CH_3SH	48.11	1.66	6	6.53	−5.5	276	NA	NA	3.9	22
Ethyl mercaptan	C_2H_5SH	62.13	2.15	35	4.45	−11.0	421	NA	300	2.8	18
Butyl mercaptan	C_4H_9SH	90.19	3.10	97	2.72	21.1	715	2	NA	NA	NA
Dimethyl sulfide	$(CH_3)_2S$	62.13	2.15	37	4.45	−9.0	423	NA	205	2.2	20
Dimethyl sulfoxide	$(CH_3)_2SO$	78.13	NA	189	4.98	−34.6	398	95	NA	[5]2.6	[5]28.5

Combustible	Formula	Mol wt	Sp gr (air = 1)	BP, °C	C_{st} (in air), vol pct	ΔH_c (25° C), kcal/mol	ΔH_c (net, 25° C), kcal/mol	Flash-point, °C	Minimum AIT, °C	Flammable limits	
										L_{25}, vol pct	U_{25}, vol pct
BORON COMPOUNDS											
Diborane	B_2H_6	27.67	0.96	−93	6.53	7.5	478	NA	40	0.8	88
Tetraborane	B_4H_{10}	53.32	1.84	16	3.67	NA	NA	NA	NA	4	NA
Pentaborane	B_5H_9	63.12	2.18	58	3.37	15.0	1,030	NA	NA	.42	NA
Decaborane	$B_{10}H_{14}$	122.22	4.23	213	1.87	8.0 (s)	NA	NA	NA	.2	NA
MISCELLANEOUS GASES											
Hydrogen	H_2	2.02	0.07	−253	29.53	0	57.8	NA	520	4.0	75
Deuterium	D_2	4.03	NA	250	29.53	0	NA	NA	NA	4.9	75
Ammonia	NH_3	17.03	.59	−33	21.83	11.0	75.7	NA	650	15	28
Carbon monoxide	CO	28.01	.97	192	29.53	26.4	67.6	NA	609	12.5	74
Natural gas (Pittsburgh)	Mixture	17	.6	NA	6.0	NA	NA	NA	500	4.8	13.5
Natural gas (others)	Mixture	17	.6–.7	NA	8.5-10	NA	NA	NA	480-630	3.8-6.5	13-17
Coal gas	Mixture	NA	.4–.5	NA	15.5-18	NA	NA	NA	NA	5.3	32

NA Not available. l liquid. g gas. s solid. oc open cup.

[1]Flammability data represent the values selected from the various publications cited in the text. The flammability limits (L_{25} and U_{25}) are mainly from references 11, 54, 72, and 110; minimum autoignition temperatures (AIT's) from references 23, 72, 110, and 112; and flashpoints from references 1, 35, 72, and 110. Flashpoints are generally closed-cup values. AIT's refer to incipient flame combustion; and L_{25} and U_{25} limits refer to combustible vapor-air mixtures at 25° ± 5° C. Most ΔH_c data are from references 91, 100, and 105 with combustible in gaseous state. Both C_{st} and ΔH_c are calculated values for ideal combustion to H_2O, CO_2, SO_2, B_2O_3, N_2, HCl, or HBr. Boiling points (BP), specific gravities (Sp gr), and molecular weights (mol wt) are from handbook references 72 and 105.

[2]Calculated.

[3]45° to 55° C.

[4]80° to 95° C.

[5]Temperature uncertain (± 25° C).

[6]100° to 115° C.

[7]120° to 135° C.

[8]160° to 175° C.

[9]140° to 155° C.

[10]200° C.

[11]90% solution.

APPENDIX B.— DEFINITION OF SYMBOLS

COMBUSTION OR THERMODYNAMIC SYMBOLS WITH TYPICAL UNITS

A — Area, m^2 or cm^2, or rate constant
AIT — Minimum autoignition temperature, °C
a — Reactant concentration, mol/L
BP — Boiling point, °C
C — Concentration, vol pct or wt pct; or specific heat, cal/(g·° C)
C_p — Heat capacity at constant pressure, cal/ (mol·° C)
C_{st} — Stoichiometric concentration, vol pct or wt pct
C_v — Heat capacity at constant volume, cal/ (mol·° C)
C/I — Combustible-inert ratio
$CO/\Delta O_2$ — Ratio of CO formation to O_2 reduction
c — Velocity of sound, m/s
c_d — Vent discharge coefficient
D — Detonation velocity, m/s
d — diameter, m or cm
E — Energy (chemical or mechanical), cal or J, or gas expansion ratio
ΔE — Energy change, cal or J
F/A — Fuel-air ratio
FI — Flammability index (fire resistance)
FS — Flame spread rate, cm/s
g — Gravitational constant, 980.6 cm/s^2
H — Heat content or enthalpy, kcal/mol
ΔH — Heat of reaction, kcal/mol
ΔH_c — Heat of combustion, kcal/mol
ΔH_f — Heat of formation, kcal/mol
ΔH_v — Heat of vaporization, kcal/mol
h — Height, m or cm
h_r — Radiative heat flux, cal/(cm^2·s)
I — Ignitor heat input, cal/cm^2, or irradiance, cal/(cm^2·s)
K — Ratio of duct area to vent area
k — Empirical constant
L — Lower limit of flammability, vol pct
L/D — Length-diameter ratio
M — Molecular weight, g/mol, or Mach number
MESG — Maximum experimental safe gap, cm
MIE — Minimum ignition energy, J
N_t — Total moles
n — Moles of a component
P_F — Fuel vapor pressure at flash point, atm or psia
P_t — Total pressure, atm or psia
P_v — Combustion pressure at constant volume, atm or psia
ΔP — Pressure rise, atm or psi
p — Partial pressure, atm or psi
Q — Heat (chemical or mechanical), cal or J
q — Rate of heating, cal/s or °C/s
R — Universal gas constant, 1.987 cal/(k·mol)
r — Radius, m or cm
S — Surface area, m^2 or cm^2
S_f — Flame speed, cm/s
S_g — Gas velocity, cm/s
S_h or S_t — Vessel hoop or tensile stress, psi
S_u — Fundamental burning velocity, cm/s
T — Temperature, °C or K
T_F — Flashpoint, °C
T_f — Flame temperature, °C or K
T_L — Lower temperature limit of flammability, °C
T_u — Upper temperature limit of flammability, °C
ΔT — Temperature rise, °C or K
t — Time, s, or thickness, cm
U — Upper limit of flammability, vol pct
V — Volume, m^3 or cm^3
v — Regression rate, cm/min, or flame velocity, cm/s

W — Weight, g or kg, and work, cal or J
X — Mole fraction
x — Distance, m or cm
Z — Rate frequency constant or compressiblity factor

GREEK SYMBOLS

α — Thermal diffusivity $\left(\frac{\lambda}{\rho C_p}\right)$, cm^2/s
γ — Ratio of specific heats (C_p/C_v)
δ_c — Vessel shape factor (thermal theory)
Θ — Reduced temperature (T/T_c)
λ — Thermal conductivity, cal/(cm·s·°C), or scaled distances, $m/kg^{1/3}$
π — Reduced pressure (P/P_c)
ρ — Density, g/cm^3
τ — Ignition delay, s

SUBSCRIPTS

1 or 0 — Initial or zero state
2 — Final state
b — Burned state
c — Critical state
f — Flame
g — Gas
i — i^{th} fraction
LL — Lower limit
m — Maximum
p — Constant pressure
T — Temperature
t — Total
u, U — Upper limit or unburned state
v — Vapor

ELECTRICAL SYMBOLS WITH TYPICAL UNITS

C — Capacitance, F
E — Voltage, V, or energy, J
I — Current, A
L — Inductance, H
Q — Electrical charge, C
R — Resistance, ohms, Ω
t — Time, s
V — Potential difference, V

APPENDIX C. — CONVERSION FACTORS

TO CONVERT FROM —	TO —	MULTIPLY BY —
Square centimeter	Square inch	0.155
Square foot	Square inch	144
Square foot	Square meter	9.290×10^{-2}
Square inch	Square centimeter	6.452
Square inch	Square meter	6.452×10^{-4}
Square yard	Square meter	0.836
DENSITY		
Gram per cubic centimeter	Pound per cubic foot	62.428
Ounce per cubic inch	Kilogram per cubic meter	1.730×10^{3}
Ounce per cubic foot	Kilogram per cubic meter	1.001
Kilogram per cubic meter	Gram per liter	1.000
Pound per cubic inch	Gram per cubic centimeter	27.680
Pound per cubic inch	Kilogram per cubic meter	27.680×10^{3}
Pound per cubic inch	Pound per cubic foot	17.28×10^{2}
Pound per cubic foot	Kilogram per cubic meter	16.018
ENERGY OR WORK		
British thermal unit (Btu)	Joules (International)	1.055×10^{3}
Btu	Calorie, gram	252.16
Btu	Foot pound	778
Calorie, gram	Joule	4.187
Erg	Dyne centimeter	1.000
Erg	Joule	1.00×10^{-7}
Foot pound	Joule	1.356
Foot pound	Btu	1.285×10^{-3}
Foot poundal	Joule	4.214×10^{-2}
Kilocalorie	Btu	3.968
Kilocalorie	Foot pound	3.087×10^{3}
Kilowatt hour	Joule	3.600×10^{6}
Watt second	Joule	1.000
ENERGY PER AREA-TIME		
Btu per square foot-second	Watt per square meter	1.135×10^{4}
Btu per square foot-hour	Watt per square meter	3.153
Calorie per square centimeter-minute	Watt per square meter	6.973×10^{2}
Calorie per square centimeter-second	Btu per square foot-second	3.690
Kilowatt per square foot	Btu per square foot-second	0.948
FLOW		
Cubic foot per minute	Cubic meter per second	4.179×10^{-4}
Cubic foot per minute	Gallon (liquid) per second	0.125
Cubic foot per minute	Liter per second	0.472
Cubic inch per minute	Cubic meter per second	2.731×10^{-7}
Pound per minute	Kilogram per second	7.560×10^{-3}
FORCE		
Dyne	Gram	1.02×10^{-3}
Dyne	Newton	1.00×10^{-5}
Gram (force)	Dyne	9.807×10^{2}
Kilogram (force)	Newton	9.807
Pound (force)	Newton	4.448
Pound (force)	Poundal	32.174
HEAT		
Btu per hour-square foot-°F	Watt per square meter-kelvin	5.678
Btu square foot	Joule per square meter	1.136×10^{4}
Btu per pound °F	Joule per kilogram kelvin	4.187×10^{3}
Btu per pound	Joule per kilogram	2.326×10^{3}
Calorie per gram	Joule per kilogram	4.187×10^{3}
Calorie per square centimeter	Joule per square meter	4.184×10^{4}
Calorie per square centimeter-second	Watt per square meter	4.184×10^{4}
Square foot per hour (thermal diffusivity)	Square meter per second	2.581×10^{-5}
LENGTH		
Centimeter	Inch	0.284
Foot	Meter	3.048×10^{-1}
Inch	Meter	2.540×10^{-2}
Meter	Inch	39.37
Micrometer	Meter	1.00×10^{-6}
Mile (statute)	Meter	1.609×10^{3}
Mile (statute)	Foot	5.280×10^{3}
Mile (statute)	Kilometer	1.609
Mile (nautical)	Meter	1.852×10^{3}
Yard	Meter	9.144×10^{-1}

TO CONVERT FROM —	TO —	MULTIPLY BY —
	MASS	
Ounce	Gram	28.35
Pound	Kilogram	45.36×10^{-2}
Slug	Pound	32.174
Ton (short, 2,000 lb)	Kilogram	9.072×10^{2}
Ton (long, 2,240 lb)	Kilogram	1.016×10^{3}
	POWER	
Btu per second	Horsepower	1.414
Btu per second	Watt	1.054×10^{3}
Calorie per second	Watt	4.184
Foot pound per second	Watt	1.356
Horsepower (metric)	Watt	7.355×10^{2}
Kilowatt	Btu per second	9.483×10^{-1}
Kilowatt	Kilocalorie per second	0.239
Watt	Joule per second	1.00
	PRESSURE OR STRESS (FORCE PER AREA)	
Atmosphere (760 torr)	Centimeter of mercury (°C)	76.0
Atmosphere	Feet of water	33.93
Atmosphere	Pound per square inch	14.696
Atmosphere	Newton per square meter	1.013×10^{5}
Bar	Newton per square meter	1.00×10^{5}
Dyne per square centimeter	Newton per square meter	1.00×10^{-1}
Inch of mercury	Pound per square inch	0.491
Inch of water (60°F)	Newton per square meter	2.488×10^{2}
Inch of water	Pound per square inch	3.609×10^{-2}
Pascal	Newton per square meter	1.00
Pound per square foot	Newton per square meter	1.488
Pound per square inch	Gram per square centimeter	70.31
Pound per square inch	Pound per square foot	144.00
Pound per square inch	Newton per square meter	6.895×10^{3}
Torr (mm Hg, 20° C)	Newton per square meter	1.333×10^{2}
	TEMPERATURE	
Celsius (T_C, °C)	Fahrenheit (T_F, °F)	$T_F = 1.8(T_C) + 32$
Celsius (T_C, °C)	Kelvin (T_K, K)	$T_K = T_C + 273$
Fahrenheit (T_F, °F)	Celsius (T_C, °C)	$T_C = (T_F - 32)/1.8$
	VELOCITY	
Foot per second	Meter per second	3.048×10^{-1}
Foot per second	Mile per hour	6.818×10^{-1}
Inch per second	Meter per second	2.540×10^{-2}
Meter per second	Foot per second	3.281
Mile per hour (statute)	Meter per second	4.470×10^{-1}
Mile per hour (statute)	Foot per second	1.467
	VISCOSITY	
Centipoise	Gram per centimeter second	1.00×10^{-2}
Centipoise	Newton second per square meter	1.00×10^{-3}
Centistoke	Square meter per second	1.00×10^{-6}
	VOLUME	
Barrel (oil, 42 gal)	Cubic meter	1.590×10^{-1}
Cubic foot	Cubic meter	2.832×10^{-2}
Cubic foot	Liter	28.316
Cubic inch	Cubic meter	1.639×10^{-5}
Cubic inch	Cubic centimeter	1.639×10^{1}
Cubic yard	Cubic meter	7.646×10^{-1}
Gallon (liquid)	Liter	3.785
Liter	Cubic centimeter	1.000×10^{3}
Quart (liquid)	Cubic meter	9.464×10^{-4}

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere
atm	atmosphere
Btu	British thermal unit
Btu/(h·ft^2)	British thermal unit per hour per square foot
Btu/lb	British thermal unit per pound
C	coulomb
°C	degree Celsius
cal	calorie
cal/cm^2	calorie per square centimeter
cal/(cm^2·min)	calorie per square centimeter per minute
cal/(cm^2·s)	calorie per square centimeter per second
cal/(cm·s·°C)	calorie per centimeter per second per degree Celsius
cal/g	calorie per gram
cal/(g·°C)	calorie per gram per degree Celsius
cal/(K·mol)	calorie per kelvin per mole
cal/(mol·°C)	calorie per mole per degree Celsius
cal/s	calorie per second
cal/ton	calorie per short ton
cm	centimeter
cm Hg	centimeter mercury (pressure)
cm/min	centimeter per minute
cm/s	centimeter per second
cm/s^2	centimeter per square second
cm^3/g	cubic centimeter per gram
cm^3/s	cubic centimeter per second
F	farad
ft	foot
ft/lb	foot per pound
ft/s	foot per second
g	gram
g/cm^3	gram per cubic centimeter
g/L	gram per liter
g/m^2	gram per square meter
gal/ton	gallon per short ton
H	henry
h	hour
in	inch
in/min	inch per minute
J	joule
J/(K·mol)	joule per kelvin per mole
K	kelvin (degree)
kbar	kilobar
kcal	kilocalorie
kcal/(cm^2·min)	kilocalorie per square centimeter per minute
kcal/mol	kilocalorie per mole
kcal/mol·K)	kilocalorie per mole per kelvin
kg	kilogram
kg/m^3	kilogram per cubic meter
km	kilometer
kpsi	kilopounds per square inch
L	liter
L·atm/(K·mol)	liter atmosphere per kelvin per mole
m	meter
m/kg	meter per kilogram
m/min	meter per minute
m/s	meter per second
mg	milligram
mg/L	milligram per liter
mJ	millijoule
ms	millisecond
μm	micrometer
mol pct	mol percent
oz/ft^3	ounce per cubic foot
pct	percent
psi	pound per square inch
psia	pound per square inch, absolute
psig	pound per square inch, gauge
psi/s	pound per square inch per second
s	second
V	volt
vol pct	volume percent
W	watt
wt pct	weight percent
Ω	ohm

U.S. GOVERNMENT PRINTING OFFICE : 1986 O - 159-315